Surface modifications of PET fabrics with low pressure plasma

by Camila Silva Flor

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SURFACE MODIFICATIONS OF PET FABRICS WITH LOW PRESSURE PLASMA

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ABSTRACT

In this study we demonstrate the feasibility of dyeing polyester with reactive dye after treatment with an argon plasma discharge. The dyeing with reactive dyes was made possible through the introduction of hydroxyl groups on a polyester fabric after treatment with low-pressure argon plasma. Additionally, a preliminary study on the effects of plasma treatment with air over polyester is presented.

The objective of this project was to modify the surface of a polyester fabric in order to improve the dyeing process. As a consequence of hydrophobicity, polyester fibers are dyed exclusively with disperse dyes. This class of dyes requires the use of temperatures up to 130°C. The research presented here addresses this limitation of the polyester dyeing process by creating a cotton-like surface over the polyester fabric. Our goal was to replace disperse dyes with reactive dyes in the polyester dyeing process. The advantage of the reactive dye process is that it is carried out at ambient temperatures.

The analytical techniques used to evaluate the results were X-ray photoelectron spectroscopy (XPS) to estimate the presence of new reactive groups in the polymer structure, atomic force microscopy (AFM), and cold-field scanning electron microscopy (FSEM) to assess topographical modifications.

Our final step was to visually prove the presence of hydroxyl groups in the fiber structure. We were able to dye the treated polyester fabrics with reactive dyes. The dyeing of plasma-treated and untreated polyester exhibited significant differences under color analysis with a spectrophotometer, with differences greater than 1, which, according to the normative *ISO 105-J03:1995*, means that the colors cannot be considered the same.

BIOGRAPHICAL SKETCH

Camila Silva Flor was born in Volta Redonda, Rio de Janeiro, Brazil on September 19, 1983. Her father is Lourival Santos Flor, a business man and Chemical Engineer. Her mother is Ana Maria do Carmo Silva, a Chemical Engineer.

Camila grew up in Barra Mansa with her grandparents Laura da Costa Silva and Joel Ozias da Silva. In Barra Mansa she attended the "Nossa Senhora do Amparo" School and spent her afternoons playing soccer. After middle school, she moved to São Paulo where she attended the "Santo Américo" School.

On September 2002 Camila moved to Spain and began her undergraduate studies as an Industrial Engineer at the "Universitat Politècnica de Catalunya" (UPC) in Terrassa, Barcelona. On January 2008 she moved to Ithaca, New York to attend Cornell University to develop her undergrad thesis. She completed her Bachelor of Science in Industrial Engineering in October 2008.

In January 2009 she started her Masters in Fiber Science in Cornell University, Ithaca.

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CHAPTER 1: BACKGROUND

1.1 Introduction

Plasma is considered the fourth state of matter. When a sufficient amount of energy is applied to a liquid it becomes a gas. Similarly, if enough energy is applied to a gas, molecules will dissociate into atoms and then into freely moving charged particles, electrons and ions, which cosntitute a plasma. A plasma is a quasi-neutral collection of charged particles and neutrals that exhibit some form of collective behavior. Particles exhibiting this behavior can interact with each other generating local electric fields. Even though the field created by each particle does not influence the whole system, such electric fields can influence the surrounding particles in a coherent way *(9)*.

Not all ionized gases fall into the plasma category. There are three basic conditions that determine whether or not a gas behaves as a plasma *(10)*. The first condition is related to the characteristic length scale in a plasma: the Debye length (λ_D). In the plasma state, particles tend to screen out the effects of charges. Opposite charges interact locally with each other, creating a cloud of oppositely charged particles around one single charge. The Debye length is a measure of the thickness of the sheath where this shielding happens. In order for a gas to behave as a plasma, then, the ionized gas dimension (L_p) must be greater than the Debye length:

$$L_p >> \lambda_D \qquad [1]$$

The formula for the Debye length is given by

$$\lambda_D = (\varepsilon_o kBT_e/e^2 n_e)^{1/2} \qquad [2]$$

where ε_o is the permittivity of free space ($8.85 \times 10^{-12} m^{-3} kg^{-1} s^4 A^2$) , k_B is Boltzman's constant ($1.38 \times 10^{-23} JK^{-1}$), T_e is the electron temperature, and n_e is the electron density. The electron density can be calculated by:

$$n_e = n_o \exp(e\Phi/KT_e) \quad [3]$$

Here n_o is the density of particles in an equilibrium situation in which $n_e = n_i = n_o$, the density of ions is n_i and Φ is the electrostatic potential in the zone where the electron density is to be calculated.

The second condition that determines whether or not a gas becomes a plasma is also related to the Debye length. If the screening process in the Debye length is to be effective, the number of particles (N_D) in a spherical Debye length needs to be greater than 1.

$$N_D = n_e (4/3)\Pi \lambda D^3 >> 1 \quad [4]$$

The third requirement for plasma creation is related to the collision frequency in an ionized gas. Collisions between molecules can decrease plasma oscillations and influence the characteristic collective behavior of a plasma. In order to behave as a plasma, a gas should have an electron collision frequency (ν_m) that is lower than the plasma frequency. The plasma frequency (f_{pe}) can be calculated with the following equation:

$$f_{pe} = \omega_{pe}/2\Pi \quad [5]$$

where:

$$\omega_{pe} = (e^2 n_e / \varepsilon_o m_e)^{1/2} \quad [6]$$

As in any gas, the temperature is defined by the average kinetic energy of particles, molecules, atoms, neutrals, or charges. Particles in a plasma will exhibit multiple temperatures unless sufficient collisions occur between the particles to attain equilibrium.

Despite the quasi-neutral characteristic of plasma, thin positive layers called "sheaths" are created when approaching the wall surfaces within which plasma is confined. The high temperature and low mass of electrons in the discharge will result in high speeds as well. For that reason, when a plasma is initiated, some electrons will be accelerated and lost to the walls. This initial situation will create an electrical potential that is positive within the plasma and falls up to zero close to the walls, hence generating the sheaths. The sheaths are responsible for keeping electrons within the plasma, accelerating them with a repulsive force directed towards the center *(1)*.

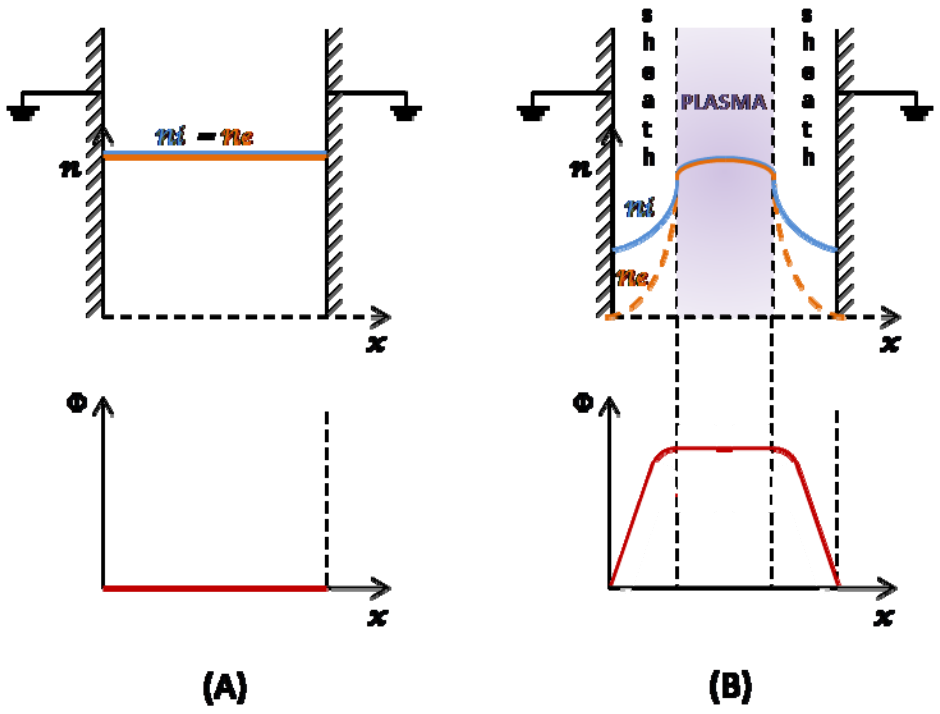


Figure 1 Formation of a sheath in a plasma. A) Initial state before sheath formation. The number of electrons and ions are the same in the whole region and the potential is zero. B) Some electrons are lost to the walls generating a positive potential in the plasma that falls to zero over the walls.*(1)*

1.2 Plasma in the textile industry

The use of plasma in the textile industry presents several advantages over traditional wet methods employed in fabric/fiber processing, not least of which is that it is considered an eco-friendly technology *(11)*. Conventional techniques require the use of great amounts of water and chemicals, generating pollution, which results in costly treatments of effluents *(12)*.

Low-pressure and atmospheric-pressure plasma are commonly used in the textile field. An important requirement in the textile industry is the production of a non-thermal, low-temperature plasma. It is a characteristic of non-thermal plasmas that their particles (neutrals, ions, and electrons) vary in temperature from one another *(13)*. In low temperature and non-thermal plasmas the gas temperature is moderate, while the temperature of the electrons is at least 10,000K. This phenomenon makes it possible for plasma to interact with the textile without degrading them.

Plasmas used for textile processing are primarily weakly ionized plasma discharges. Some of the main characteristics of these types of discharges include that they are controlled electronically; the temperatures of different particles are different; the collisions between electrons and neutrals are very important to maintain the plasma since the ionization of neutrals by electrons sustain the plasma; and surface losses of particles at some boundaries can influence the plasma very much.

The ionization friction of a plasma can be calculated with the following formula:

$$x_{iz} = n_i/(n_g + n_i) \qquad [7]$$

where n_g is the neutral gas density.

If $x_{iz} << 1$, the plasma is considered weakly ionized.

1.3 Types of plasmas used in the textile industry

Plasma systems used in textile industry can be separated into two groups: systems that work at low-pressure or vacuum conditions and the ones that produce plasma at atmospheric pressure.

1.3.1 Low pressure vacuum plasma

In a vacuum system the pressure employed to obtain a plasma depends on the frequency of the electromagnetic energy applied to the gas. To induce a plasma by radio frequency (RF), the working pressure is approximately 0.1mbar, whereas in a microwave-driven plasma the pressure ranges from 0.5 to 1mbar. However, pressures of approximately 0.01mbar are required to obtain a more controlled plasma *(10)*. The density of particles in a lab plasma ranges from $10^{9}cm^{-3}$ for diffuse systems such as Plasma-Enhanced Chemical Deposition (PECVD) to $10^{26}cm^{-3}$ for dense plasma systems *(1, 9)*.

Low-pressure plasma treatments over textiles are commonly aimed at surface activation, etching, cleaning, and coating deposition.

The use of vacuum technologies in the textile industry has some disadvantages, one of the most important of which is that they are batch processes and therefore cannot be run as a continuous line. However, batch processes also have some positive outcomes. The complete manipulation of a textile product is not carried out in one single, continuous step, but rather consists of a series of discrete batch processes. Therefore the use of plasma machine would involve only one more batch system that composes the line. Moreover, if there happens to be a breakdown in the line that stops the plasma machine, the costs associated with such a breakdown would be higher than if it were composed of batch systems, because the cost of not operating the plasma machine would be relatively high. Finally, it is possible to use a roll-to-roll system that

permits the loading of a considerable amount of fabric or yarn. In this case there would be no need for a continuous reload of the textile into the machine *(10)*.

Contrary to common belief, low-vacuum plasma treatment, especially when it involves roll-to-roll equipment, is a highly cost-effective technology. The typical cost for plasma activation is in the range of 0.01 to 0.02€/m^2 *(10)*.

1.3.2 Atmospheric plasmas

The types of atmospheric plasmas used in the textile industry are the corona discharge, the dielectric barrier discharge (DBD) and the glow discharge plasma.

1.3.2.1 Corona discharge

A corona discharge usually occurs in regions of sharp, non-uniform electric fields *(13)*. In this type of plasma the discharge is generated from a strong electric field surrounding a conductive tip. A plasma formed by a corona discharge is weakly ionized, with a free electron density of approximately 10^8electrons/cm^3 *(10)*. Because it is unlikely for a plasma to form a corona discharge without the presence of an asymmetrical electric field around a singularity, the resulting plasma is usually non-uniform. An illustration of the initiation process is shown in Figure 2 *(14)*.

In a plasma apparatus for textile modification, a corona discharge machine would usually contain several needles, as shown in Figure 3.

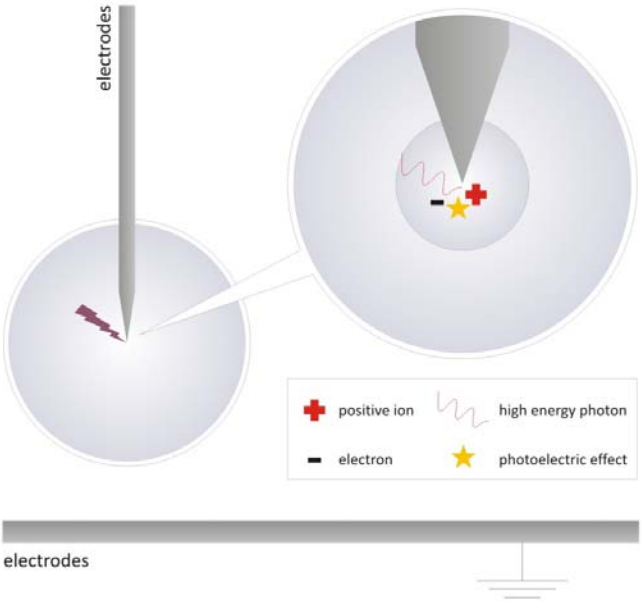


Figure 2 Corona discharge initiation. The discharge is formed due to the presence of an electric field around a singularity, in this case represented by the tip of the electrode.

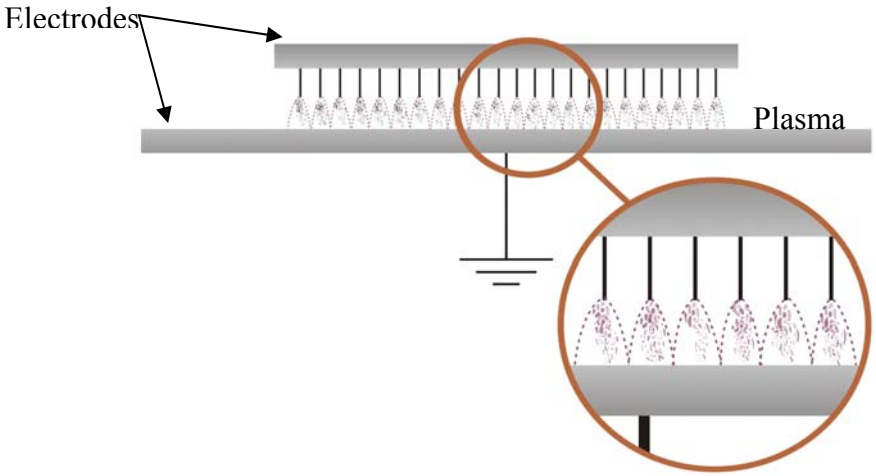


Figure 3 Plasma formed with a corona discharge. Several needles in parallel compose a typical apparatus. The discharges are generated from the needles generally creating a non-uniform plasma.

1.3.2.2 Dielectric Barrier Discharge (DBD)

In a dielectric barrier discharge (DBD), a plasma is generated between two symmetric conductive plates, where the breakdown of the gas is induced by applying high voltage. In order to avoid an electrical current arcing from one electrode to the other, which may burn the sample, the plates are covered with a dielectric material (ceramic or glass). The dielectric coating spreads the charge over the plates, inhibiting the formation of arcs. A DBD is characterized as a large-area, non-thermal, uniform type of plasma. Compared with a corona discharge, DBD has a higher electron density ($\sim 10^{10}$electrons/cm^3) and slightly cooler electron temperature. However electron temperature is not the only important concern in DBD discharges. All particles in contact with a sample are important. In the textile industry cold plasma processes are favored over high-temperature processes because the latter induce degradation of fibers *(10)*.

The most common DBD type is filamentary, where the plasma looks like an array of microdischarges. Because of the short duration of such microdischarges there is not enough time to heat the gas. Therefore the temperature of the whole system (including all species in the plasma) is not high enough to degrade the fiber. The electron temperature in a DBD discharge ranges from 10,000K to 100,000K, while the gas remains at a moderate temperature (at most 100°C) *(10)*. A graphic representation of a DBD system can be observed in Figure 4 *(15)*.

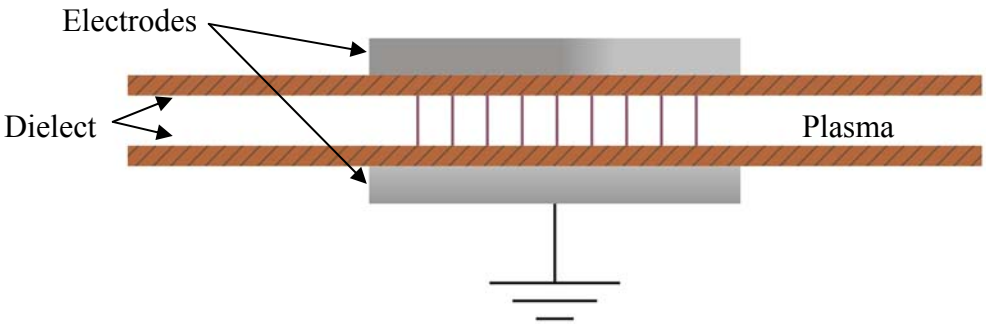


Figure 4 Plasma generated with a dielectric barrier discharge. Plasma is formed between the dielectric plates. The role of the dielectric material is to spread the charges resulting from the breakdown of the gas, generating an uniform cold plasma.

1.3.2.3 Glow Discharge

An atmospheric pressure plasma glow discharge is a uniform and homogeneous method of producing a plasma. In such a discharge the voltage applied is around 200V, which is lower than is characteristic of other types of plasmas. Compared with DBD and corona discharge, this method uses a higher frequency and exhibits a higher electron density (~ 10^{11}-10^{12} electrons/cm^3). In glow discharge the electrodes are made of metal, which deliver power densities of about 500W/cm^3. This amount of power makes the high density of free electrons possible. Additionally, the electrons produced exhibit temperatures of 10,000K to 20,000K. The fact that glow discharge is a low-temperature plasma process enables its use in the textile industry, where degradation of the material caused by temperature is an important issue *(10)*. A schematic diagram of a glow discharge setup is shown in Figure 5.

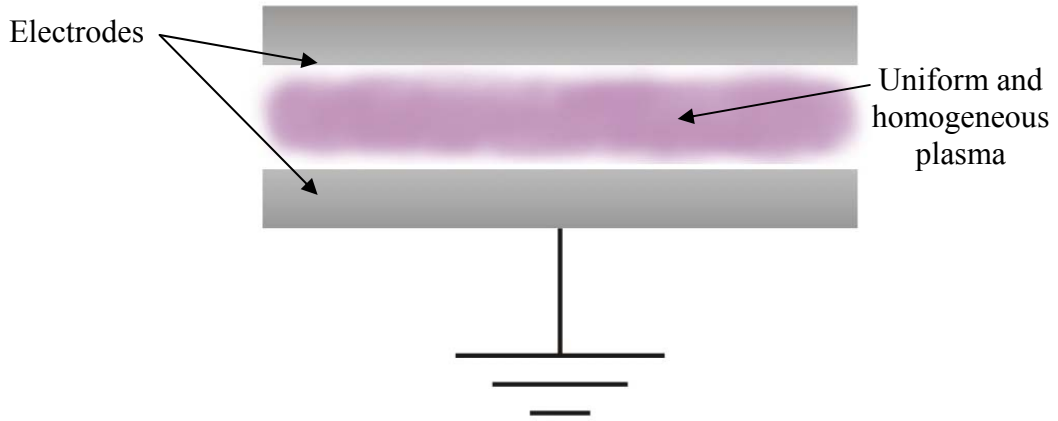


Figure 5 Plasma formed with a glow discharge. High frequency (RF) is applied to the electrodes in the system, generating plasma with high electron density. This results in an uniform and homogeneous plasma.

In order to control arcing from one electrode to the other in a glow discharge system, helium is used during plasma formation as the carrier gas. Helium is an inert gas known as a good plasma initiator. Helium is a simple atom with only two electrons and a very simple structure. As a consequence, it is restricted in terms of its options for releasing energy once excited. It does not, for example, exhibit modes of vibration or rotation like an oxygen atom does. The easiest way for a helium atom to spend the energy received is ionizing. Therefore, helium is the most common gas used to initiate plasmas and to control plasmas produced by glow discharges *(10)*.

A comparison between the three atmospheric plasma systems used in the textile industry is presented in Table 1.

Table 1 Comparison between atmospheric plasma systems

PARAMETERS	Corona discharge	DBD	Glow discharge
Voltage	~50kV/cm at a radii between 2-10mm (continuous or pulsed)	Ac: 1-20kV	Ac: ~200V
Frequency	-	1-100kHz	2-60MHz
Electron density (electrons/cm^3)	10^8	10^{10}	$10^{11} – 10^{12}$
Electron temperature (K)	>100000	20000 - 50000	10000 – 20000

1.3.3 Applications of plasma treatments over polyester

Polyester (PET) is a fiber with many special characteristics, including outstanding mechanical and chemical properties. PET is one of the most often used fibers, with applications ranging from apparel textiles to construction to the medical field to automotive parts to agriculture *(16)*. With respect to some applications, however, the low hydrophilicity of polyester can become a major weakness. As an example, when processing polyester in the apparel industry, it is necessary to increase the wettability of the fabrics as most of the processes are realized in water solution.

Plasma modification of polymers has been employed as a powerful tool to obtain desirable surface characteristics without interfering with the bulk properties of materials. Noticeably, cold plasma treatment of polyester has been widely studied by many researchers, who have reported various types of modifications for numerous applications.

A variety of modifications have been carried out over polyester **films**. By using a remote plasma system that irradiates only radicals under vacuum while employing ammonia as the gas, Narushima *et al.* were able to introduce nitrogen groups over PET (poly(ethylene terephthalate)) films*(17)* and used XPS analysis to detect the nitrogen. In another experiment Narushima *et al.* introduced nitrogen groups onto fabrics by

irradiating them with argon plasma in combination with a solid-phase monomer deposition. The monomers used were allylbiguanide hydrochloric acid salt (ABG), N-methylol acrylamide (NM-AAm) and N-isopropyl acrylamide (NIP-AAm) *(18)*. Gupta *et al.* introduced oxygen-containing groups over PET films with RF argon plasma followed by air exposure, and also used graft polymerization of acrylic acids after argon plasma in other experiments with protein immobilization and cell seeding *(19-21)*. Charpentier *et al.* imparted hydrophilicity to a polyester vascular prosthetic device using an air RF low-pressure plasma system *(22)*. According to XPS analysis there was an increase in the oxygen concentration in the form of C–O(H) on the treated polyester surfaces of the medical devices. More recently, researchers have begun working with plasma treatments over **fibers and fabrics**. The objective of this treatment ranges from increasing the fabric's hydrophilicity or hydrophobicity to improving its color depth after dyeing. For example, Selli *et al.* imparted **hydrorepellence** to PET fabrics using a sulfur hexafluoride (SF_6) vacuum plasma treatment *(23)*. For the characterization of the modified PET they used X-Ray photoelectron spectra (XPS), Electron paramagnetic resonance (EPR), Differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), water contact angle and water droplet roll-off angle (WDRA) measurements. Water contact angle and WDRA were used to find the optimum experiment conditions. EPR results indicated the formation of organic radicals on carbon atoms while XPS analysis showed that PET's hydrorepellence was strongly related to the presence of fluorine on the polymer surface. XRD and DSC results before and after the treatment did not present any differences. Lei *et al*. copolymerized hydrogen silicon fluid (HSF) over a PET fabric with a corona discharge plasma treatment. Characterization of the modified fabric was carried out by contact angle measurement, Electron spectroscopy for chemical analysis (ESCA), water impact

penetration test, scanning electron microscopy (SEM) and tensile strength measurement. The results showed that the longer the plasma treatment the higher the degree of grafting obtained. *(24)*. Several studies have reported the ability to increase polyester **hydrophilicity** with a plasma treatment, which is an essential property to achieve PET dyeing *(25-27)*. Wei *et al.* improved the wettability of PET fibers using a low-pressure plasma treatment with oxygen. Topographical modifications of the PET fibers were studied using atomic force microscopy (AFM) and the introduction of functional groups was analyzed with XPS. After plasma exposure the PET fibers presented a new C=O peak confirming the presence of new functional groups *(28)*.

Plasma treatments have also been applied with other finishing purposes. Qi *et al.* treated PET fibers with oxygen low-pressure glow discharge plasma in order to increase the adhesion of a **self-cleaning finish** (anatase TiO_2) *(29)*. Simor *et al.* used nitrogen plasma to impart hydrophilicity to polyester in order to facilitate the absorption of a palladium catalyst, which provides a catalytic surface for nickel electroless deposition *(30)*. Keller *et al.* tested three types of plasma against conventional textile processes for the removal of sizing agents from polyester yarns *(31)*. Keller's results showed that low-pressure plasma removed 4.4 weight% of the sizing agent and did not degrade the fiber like the two other methods used: atmospheric and low-pressure microwave plasmas. Titov *et al.* studied the influence of plasma in the texture of polyester fabrics. They evaluated the rates of mass loss, oxygen uptake, and gases produced after air plasma treatment over PET films and fabrics with various specific surface areas *(32)*. By periodically weighting the samples, they concluded that the rate of mass loss in PET fabrics was lower than it is in films, where a higher outer surface of the polymer is exposed to plasma.

Since the development of polyester one of the biggest challenges has been coloring it *(33)*. After several trials, disperse dyes were used for dyeing PET. In the

disperse dyeing method, the dye does not react with the fiber but it is dispersed in water to further penetrate into the polymer structure. A few years ago, dyeing of polyester was usually done with the addition of carriers that accelerated the process *(33)*. Carriers are molecules such as o-phenylphenol (2-hydroxybiphenyl) which are used as solubilizing agents that swell the fiber in the bath, facilitating the diffusion of the dye into the amorphous zone of polyester. Due to environmental concerns the use of carriers was replaced by high-pressure processes (up to 5barr). These processes became the regular procedure for dyeing polyester up to now.

In a high-pressure dyeing process a machine called an *autoclave* is used. The autoclave works at temperatures above the fiber's glass transition temperature (T_g). The Tg for polyester varies between 130°C and 150°C, requiring a great amount of energy for the dyeing process. Therefore polyester dyeing is still an expensive process that involves a considerable amount of energy.

Several attempts have been made to alter the polymer structure and improve the dyeing process of polyester. Researchers have tried to modify polyester before extrusion and have developed anionic and cationic dyes to react with the modified PET *(34)*. More recently researchers have employed plasma treatments to find a way to overcome the large amount of energy required for PET dyeing. For example, Öktem *et al.* **improved the dyeability** of PET fabrics with basic dyes *(35)*. They used corona discharge plasma with argon and acrylic acid polymerization. By following a similar technique—plasma treatment with in situ acrylic acid polymerization—Ferrero *et al*. were also able to improve PET dyeability with basic dyes, however the dyeing presented unsatisfactory fastness after washing*(36)*. Addamo *et al*. increased the dyeability of PET fibers with disperse dyes after a treatment with RF air plasma *(37, 38)*. Other efforts were carried out in order to increase the color depth of fabrics. As an example, Lee *et al.* applied a plasma treatment under atmospheric pressure with

deposition and polymerization of an anti-reflective resin over PET fabrics. Hexamethyldisilane (HMDS) and tris(trimethylsilyloxy)vinylsilane (TTMSVS) organic compounds were used for the coating. The carrier gas employed was a mixture of oxygen and helium *(39)*. Lehocky and Marek were able to obtain the same reflectance that a regular dyeing process yields after dyeing without the use of sodium sulfate. An RF plasma reactor with air was employed for the treatment before dyeing. XPS analysis showed an increase in the oxygen to carbon and nitrogen to carbon ratios with treatment time, however the individual values of the analysis were not presented*(40)*. Zhang et al. improved PET's color yields in inkjet printing after plasma exposure with air and argon *(41)*. The present study aims at improving the dyeing process of polyester by employing a different type of dye in the process. For this, our first step was to modify the fiber surface by means of a plasma treatment so it would be able to react with the dyes.

CHAPTER 2: SURFACE MODIFICATIONS OF PET FABRICS WITH LOW PRESSURE AIR PLASMA.

2.1 Introduction

In this work we report the modification of a polyester fabric surface using an air plasma treatment. Four different types of dyes (reactive, disperse, acid, and basic) were used in order to evaluate the reactivity of the plasma-treated polyester.

2.2 Experimental

2.2.1 Materials and equipment

- Fabric

Fabrics of 100% polyester (0.014g/cm^2) comprised of 76% yarn 165/72 with 1000 twists and 24% yarn 78/24 (unifi bright) from Fibra S/A - Brazil were employed. The fabrics were previously purified with 2,0g/L of detergent (Goldpal VP from Golden Quimica - Brazil) and 0,5g/L of acetic acid (from Labsynth - Brazil) for 30 minutes at 80°C.

- Dyeing supplies

The dyes employed were Disperse Red E-2BL 200% and Reactive Red BG-3B, both from Golden Quimica – Brazil, Texacryl Red GRL from Texilon – Brazil and Nylosan Red EBL from Clariant. Ammonium sulphate, acetic acid, ammonia, sodium hydrosulfite and sodium acetate were obtained from Labsynth - Brazil. The leveling agent (Goldgen PA) and the dispersing agent (Goldsperse NG) were acquired from Golden Quimica – Brazil. Sodium chloride was obtained from Quinesp - Brazil, sodium carbonate from Brenntag – Brazil and caustic soda from UNIPAR, União de Industrias Petroquímicas S.A – Brazil.

All dyeing processes were realized in a high temperature beaker dyer model ALT-I from Mathis – Brazil.

- Plasma reactor

A PLASMA-PREEN 1 (Plasmatic Systems, Inc.; North Brunswick, NJ) microwave oven plasma reactor was employed. The plasma system was equipped with a quartz-made barrel type process chamber that measured 4.1 inches in diameter and 6.0 inches long as seen in Figure 6.

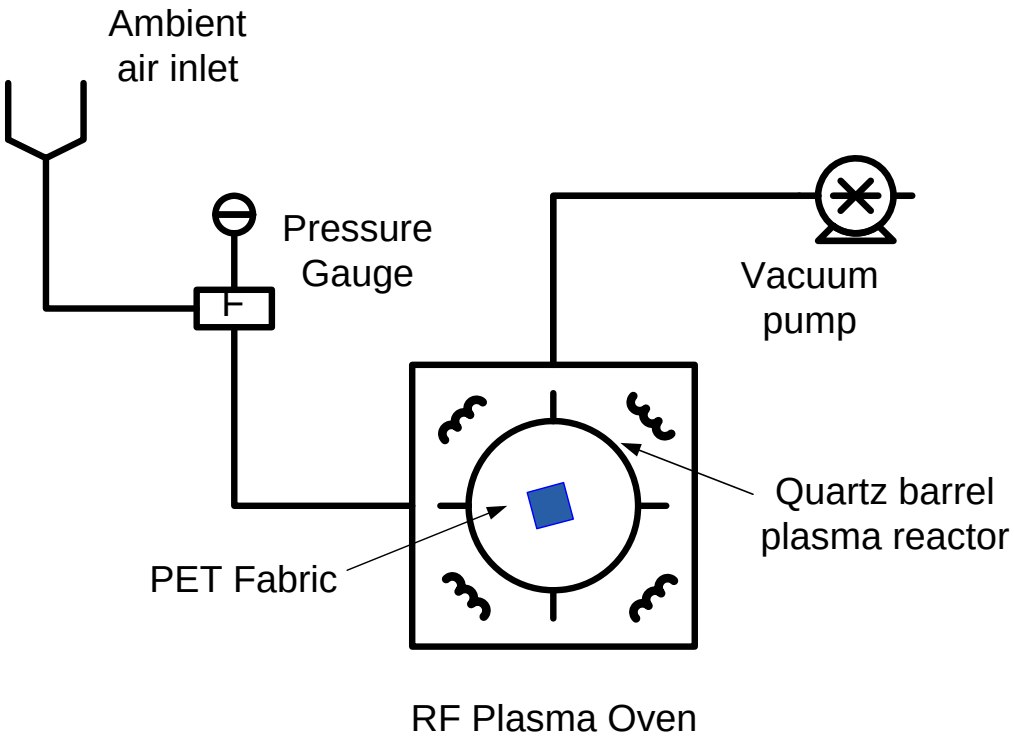


Figure 6 Plasma processing chamber. Plasma is generated in the chamber with the energy supplied form the microwave oven.

The PLASMA-PREEN 1 system works by streaming gas into the chamber at reduced pressures (<5Torr). The plasma discharge is formed by the microwave energy

generated in the microwave oven. The process produces a weakly ionized plasma with active species that will react with the sample in the chamber *(35)*. The PLASMA-PREEN 1 has a power range of between 100 and 750 watts and operates at 2.45 GHz. The polyester fabric was placed into the glass chamber and then treated using ambient air. Aalborg mass flow-meter/controllers were used to measure and control the gas flow rate.

The pressure within the chamber was measured with a Supco VG64 digital vacuum gauge. The glass reactor was pumped using a Precision Scientific vacuum pump from Pfeiffer Vacuum (DUO 2.5 Mod No. PK D41 707C).

2.2.2 Plasma treatment and analysis

PET fabrics were cut into 7cm x 12cm pieces and treated under a flow of approximately 120sccm of air plasma at 750W under ambient temperature. The fabric was introduced into the chamber, which was evacuated up to a pressure of 0.76mTorr. Following this step, the air flow was pumped into the chamber, the working pressure was adjusted, and plasma was initiated. After the treatment the pressure in the chamber was released and the sample removed. The treated fabrics were kept separately in Ziploc bags for further analysis.

The first set of experiments consisted in determining the optimal pressure for the experiments carried out in this study. Time and pressure were varied according to Figure 7. Once the most suitable pressure was chosen, all experiments were realized through five exposures to plasma of increasing lengths: 10, 30, 60, 120, and 150 seconds.

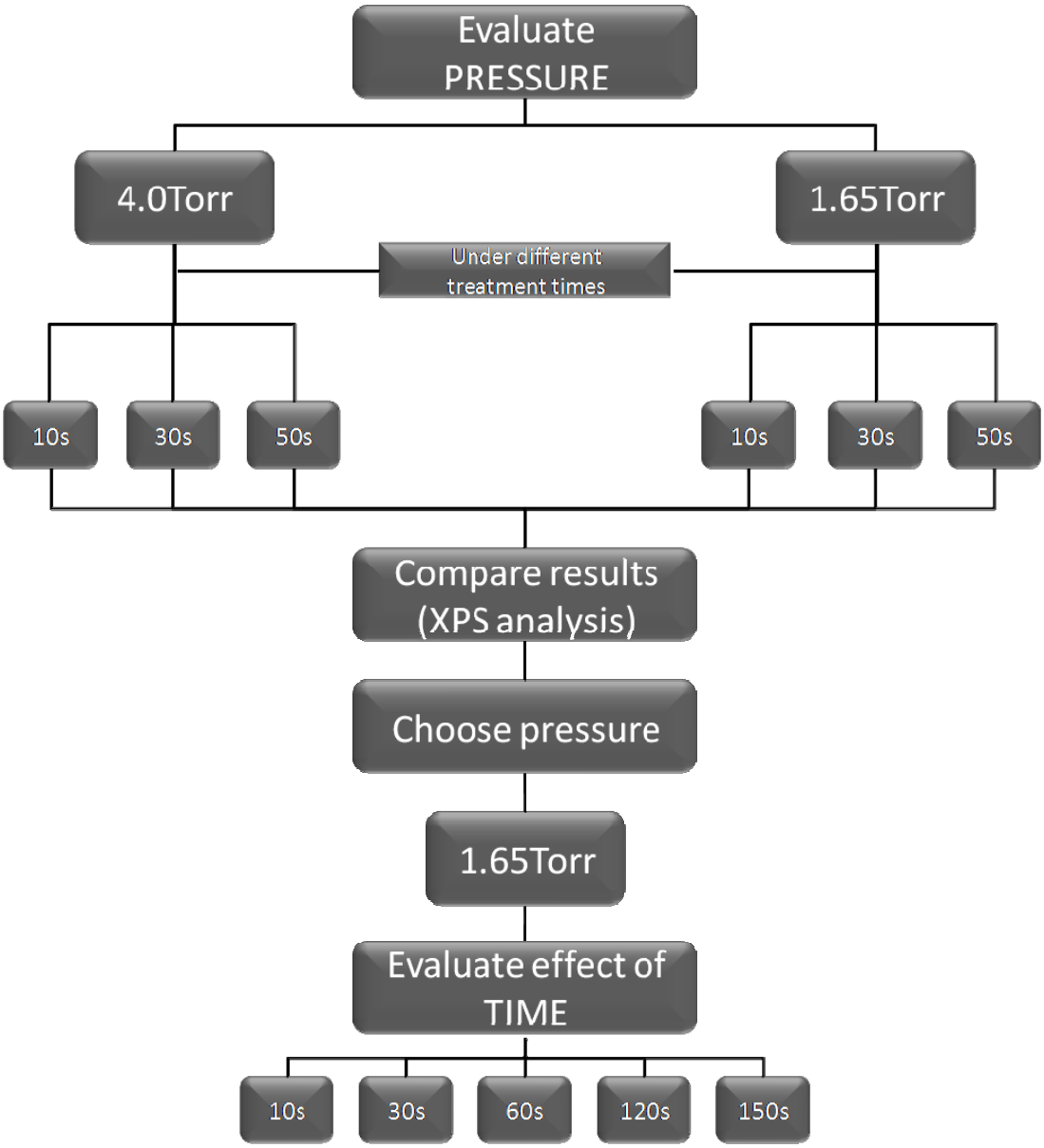


Figure 7 Planning of experiments. The first step was to choose the optimal pressure for the experiments. The trials with 4.0 and 1.65Torr of pressure were conducted using three exposure times (10, 30, and 50 seconds). After the optimal pressure was chosen—in this case 1.65Torr—the exposure time was evaluated. For time evaluations, five periods were used (10, 30, 60, 120, and 150 seconds).

2.2.3 X-ray Photoelectron Spectroscopy (XPS)

XPS spectra were obtained on an SSX-100 system equipped with a hemispherical analyzer and a monochromatic Al Kα x-ray source with 1486.66eV of energy. The analyzer pass energy was 150V for survey scans and 50V for high-resolution scans. Photoemission electrons were collected from the sample at a 55-degree emission angle. The beam spot was 1mm in diameter, incident on the sample at 55 degrees from surface normal, which resulted in an ellipse of about 1mm x 2mm. The operating pressure was around $2x10^{-9}$Torr.

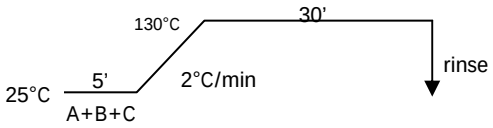
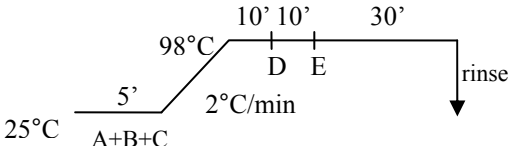
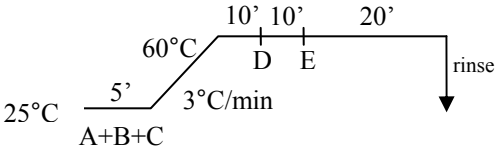
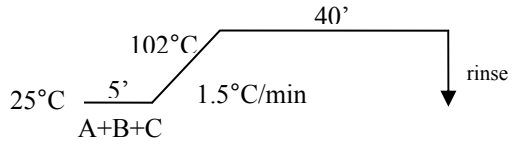
2.2.4 Hydrophilicity tests

Two pieces of fabric (plasma-treated and untreated) of the same dimensions were suspended over a plate with a blue dye in aqueous solution. The dye solution contained approximately 1g/L of methylene blue for visual evaluation of water absorption into the fabric. The two pieces of textile were put in contact with the solution, absorbing it vertically.

2.2.5 Dyeing procedures

The dyeing procedures followed are explained in Table 1.

Table 2 Dyeing Processes with disperse, acid, reactive and basic dyes

Class and type of dye	Process	Products
Disperse: *Red E-2BL 200%*		A: 2% owf dye B: 2g/L ammonium sulphate C: acetic acid (pH 5.0 – 5.5)
Acid: *Nylosan Red EBL*		A: 0.2% owf dye B: 2.0% leveling agent C: ammonia (pH 8.5 – 9.0) D: 2g/L ammonium sulphate E: 0.5g/L acetic acid
Reactive: *Red BG-3B*		A: 0.2% owf dye B: 1.0g/L dispersing agent C: 15g/L sodium chloride D: 5g/L sodium carbonate E: 0.15g/L NaOH
Basic: *Texacryl Red GRL*		A: 0.2% owf dye B: 0.5g/L sodium acetate C: acid acetic (pH 4.0 – 4.5)

2.2.5.1 Dyeing process with disperse dyes

For the dyeing process with disperse dye an aqueous solution with 0.2% over weight of fiber (owf) of the dye and 2g/l of ammonium sulphate was used. Acetic acid was employed for pH adjustment (5.0 – 5.5). The dye, salt, and acid were all mixed and the solution was stirred constantly for 5 minutes at 25°C. After this step, the temperature was increased to 130°C at 2.0°C/min. Once the solution temperature reached 130°C, the fabric was immersed and the bath was kept at a constant temperature of 130°C for 30 minutes. The solution was then cooled and the fabrics rinsed for 15min.

2.2.5.2 Dyeing process with acid dyes

For the dyeing process with the acid dye, 2.0% of a leveling agent for polyamides, 0.2% owf of acid dye, 2.0g/L of ammonium sulphate and 0.5g/L of acetic acid were employed. Ammonia was employed for pH adjustment (8.5 – 9.0). The leveling agent, the dye, and the ammonia were added to the bath and stirred constantly for 5 minutes under ambient temperature. The bath was then heated to 98°C at 2.0°C/min. After 10 minutes of constant stirring at 98°C, the ammonium sulphate was added followed by acetic acid. The mixture was stirred constantly for 30 minutes followed by cooling and rinsing of the fabrics.

2.2.5.3 Dyeing process with reactive dyes

For the dyeing process with reactive dye an aqueous solution with 0.2% owf of the dye, 1g/L of dispersing agent, 15g/l of sodium, 5g/l of sodium carbonate and 0.15g/L of caustic soda 50°Be were used. The dispersing agent, the dye and sodium chloride were added to the bath in the beginning of the process and stirred constantly for 5 minutes under ambient temperature. The bath was then heated to 60°C at

3.0°C/min. After 10 minutes at 60°C, the sodium carbonate was added. Ten minutes after the addition of sodium carbonate, the caustic soda was added. The solution was stirred constantly for 20 more minutes and then was cooled and the fabrics were rinsed.

2.2.5.4 Dyeing process with basic dyes

The dyeing process with the basic dye was done with 0.2% owf of dye and 0.5g/L of sodium acetate. Acetic acid was employed for pH adjustment (4.0 – 4.5). The reactants were added to the bath and the solution was kept for 5min at room temperature with constant stirring. The bath was then heated to 102°C at 1.5°C/min and kept at that temperature for 40 minutes with constant stirring. The solution was then cooled and the fabrics were rinsed.

The dyed fabrics were washed with a reductive solution of water containing 2,0g/L of sodium hydrosulfite and 2,0g/L of caustic soda 50°Be to remove any residual dye from the fiber surface.

2.2.5.5 Rinsing process

The process of washing was as follows: First the fabric was introduced in a bath with 1/3 of the caustic soda at ambient temperature. The bath was warmed at 3°C/min until it reached 80°C. At 80°C, 1/3 of the caustic soda and ½ of the sodium hydrosulfite were added and stirred constantly for 15 minutes. The remaining caustic soda and sodium hydrosulfite were then added and stirred constantly for 15 more minutes. Following this step, the fabric was washed in water for 10 minutes. Finally, the fabric was washed in a solution containing 0.5g/L of acetic acid at 50°C for 10 minutes and then with water only for 10 more minutes.

2.3 Results and Discussion

2.3.1 Surface characterization

Modification of the surface induced by plasma treatments were analyzed using x-ray photoelectron spectroscopy (XPS). Figure 8 shows variations in oxygen and nitrogen content in PET fabrics treated under various pressures and times. The control sample is shown in green, which corresponds to the XPS of a polyester fabric before plasma treatment.

Due to the higher stability of plasma at 1.65Torr as well as the superior amount of nitrogen and oxygen groups in the polyester fabric after treatment, 1.65Torr was chosen as the optimal pressure for further experiments.

In Figure 9 it is possible to see an increase in the oxygen and nitrogen groups with increasing treatment time. All experiments were carried out at 750W with an air flow of 120sccm at ambient temperature. For each fabric, three random points of the surface where chosen for XPS analysis in order to confirm the uniformity of the treatment. Additionally, each treatment was repeated three times in order to test reproducibility.

A hypothesis explaining how oxygen and nitrogen are being introduced in the PET structure is based on the work of Weidner *et al*. and Gheorghiu *et al. (2, 3)*. These researchers studied the degradation products from polyester after oxygen plasma treatment. Some of the products from degradation of PET in an oxygen discharge presented by Weidner *et al*. and Gheorghiu *et al.* are shown in Figure 10.

We believe that oxygen in the air can produce a similar effect, creating radicals and introducing new reactive groups to the fiber. To support this theory, our XPS results, as presented in Figure 14, show that there was an increase in carboxylic groups on the polyester fabric.

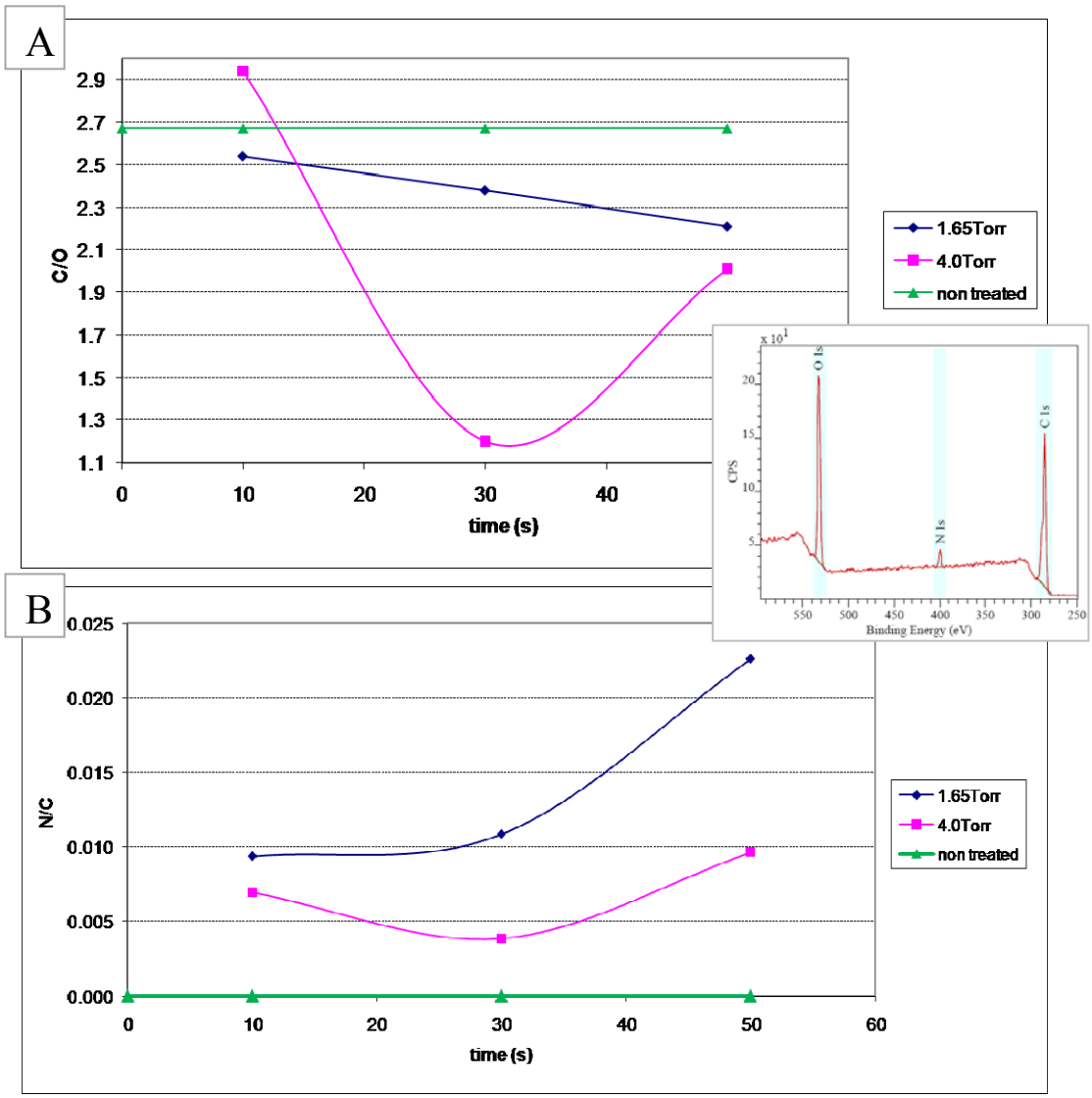
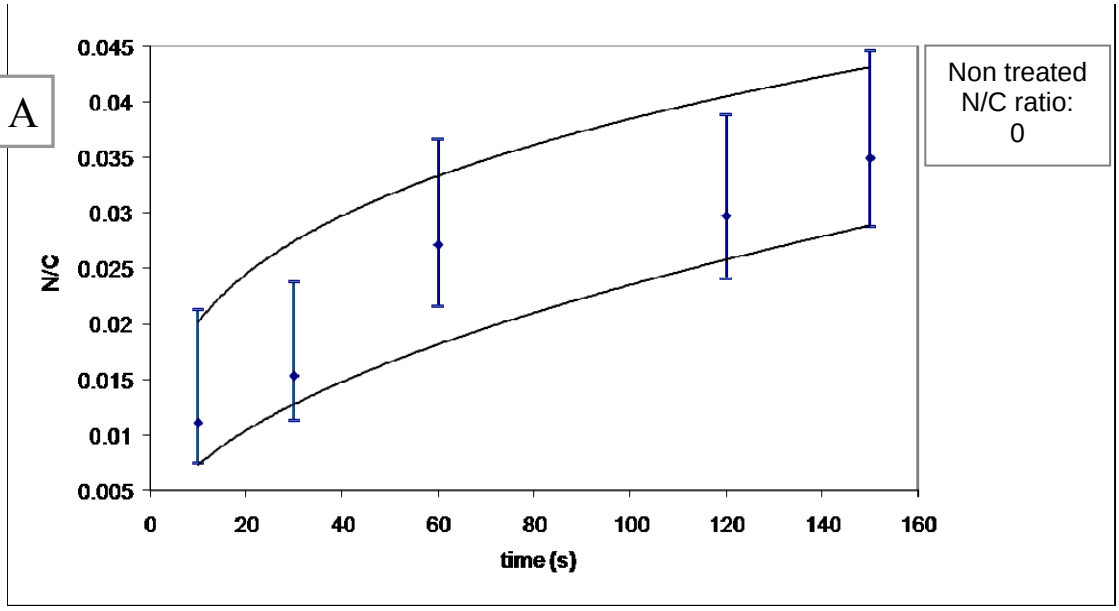


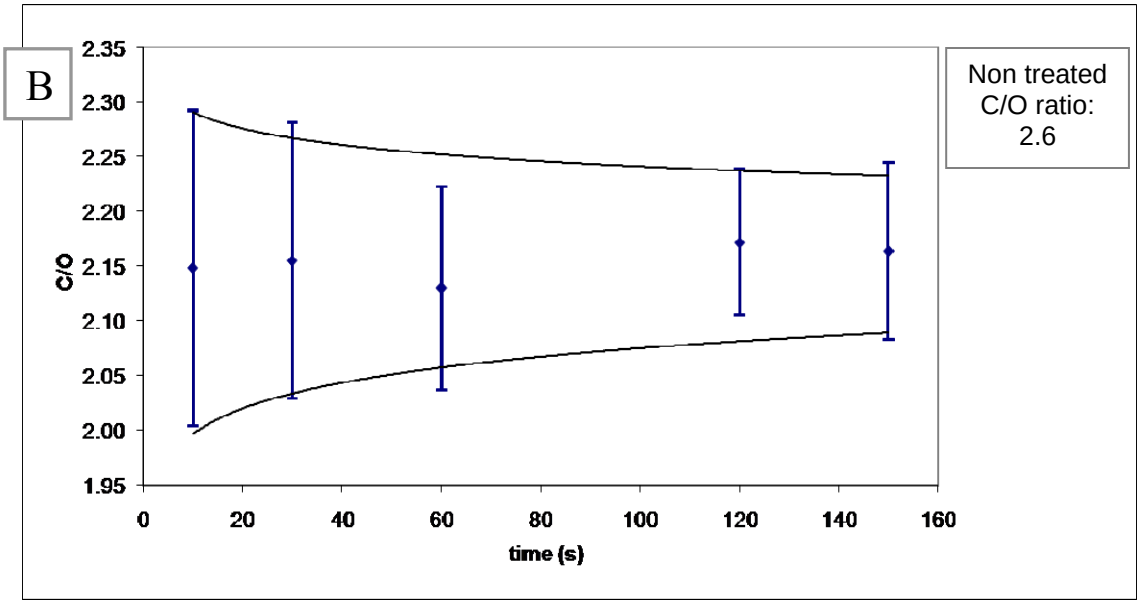
Figure 8 Analysis of oxygen and nitrogen introduction when varying the pressure and duration of the plasma treatment. A) Oxygen analysis: at 4Torr of pressure the plasma was unstable as black shades in the plasma were observed. As a consequence of this instability, the ratios of C/O at 4.0Torr did not exhibit any pattern with increasing treatment time. The presence of oxygen groups in polyester at 4Torr was very irregular. When 1.65Torr of pressure was used the plasma became more stable, presenting a uniform violet color. The stable plasma resulted in a uniform treatment, a finding that can be corroborated by the amount of oxygen present in the polyester chains observed with the XPS. With longer plasma treatments the C/O ratio decreased in an almost-linear pattern, indicating an increase in the amount of introduced oxygen. B) Nitrogen analysis: at 4Torr of pressure the generated plasma was not stable. Even though it was possible to observe a similar trend in the results for both pressures, when 1.65Torr of pressure was used the resulting concentration of nitrogen was higher than that for the experiments with 4.0Torr. The higher N/C ratios with 1.65Torr might be related to greater plasma stability at this pressure.

Figure 9 Introduction of reactive groups in polyester chains. A) Oxygen analysis. The longer the plasma treatment, the more uniform was the introduction of oxygen groups along the fabric. The C/O ratios did not present significant changes for longer plasma treatments, as observed in the mean value of the ratios at various treatment times. However, when compared with untreated polyester, the reduction in the C/O ratio after treatment was approximately 17% (from 2.6 to 2.15). B) Nitrogen analysis. Despite being smaller than the amount of oxygen, nitrogen groups were also introduced in the polymer chain. It is possible to observe two different regimes in the graph: a linear growth pattern from 10 to 60s and a constant ratio after 60s. We believe that in the first regime (10 to60s) nitrogen ionization from the air did not achieve its maximum value, and therefore the amount of nitrogen available to react with the polymer was variable. After 60s of treatment, the density of ionized nitrogen stabilized, resulting in more constant N/C ratios. Compared with oxygen, which has an ionization energy of 12.5eV and presented more-or-less constant C/O ratios under all treatment times, the energy required to ionize nitrogen is relatively high (14.53eV). This difference in energy would explain the presence of two behaviors observed in the N/C evaluation graph, while in the C/O analysis the ratio was approximately constant.

A


0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
N/C
0
20
40
60
80
100
120
140
160
time (s)
Non treated
N/C ratio:
0

B


2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
1.95
C/O
0
20
40
60
80
100
120
140
160
time (s)
Non treated
C/O ratio:
2.6

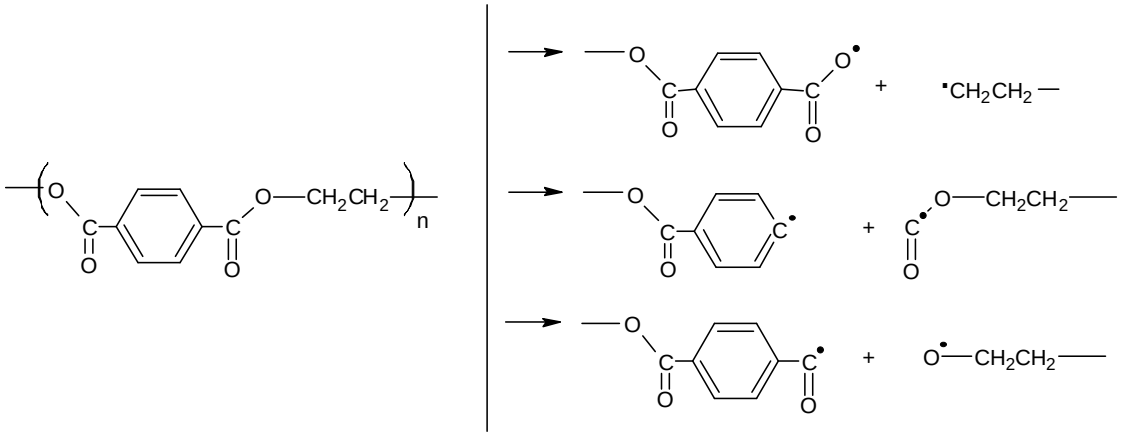


Figure 10 Degradation products from a PET after an oxygen plasma treatment. *(2, 3)*

Our supposition is that the oxygen is breaking the ester chains, producing COOH groups. In contrast, we assume that the ionized nitrogen could have reacted with the radicals created due to PET degradation in plasma. The analysis of the types of nitrogen groups that were introduced was realized based on the XPS results. According to findings in the literature, nitrogen elements as part of amine groups are positioned around 399.1eV while amide groups are found around 399.9eV *(42, 43)*. In our case it is possible to notice in Figure 11 that the nitrogen peak appears at 399.98eV. We believe therefore that the nitrogen groups created are amides.

The evaluation of the types of oxygen groups that were created on the fabric surface was carried out by deconvoluting the carbon and oxygen peaks in the XPS analysis of the spectra.

Three types of bonds are observed for carbon atoms in polyester, as shown in Figure 12: Carbon number 1 corresponds to the carbon in the aromatic ring, carbon number 2 is bonded on one side to the oxygen in the ester group and on the other side is part of the aliphatic chain, and carbon number 3 is part of the ester group in the chain.

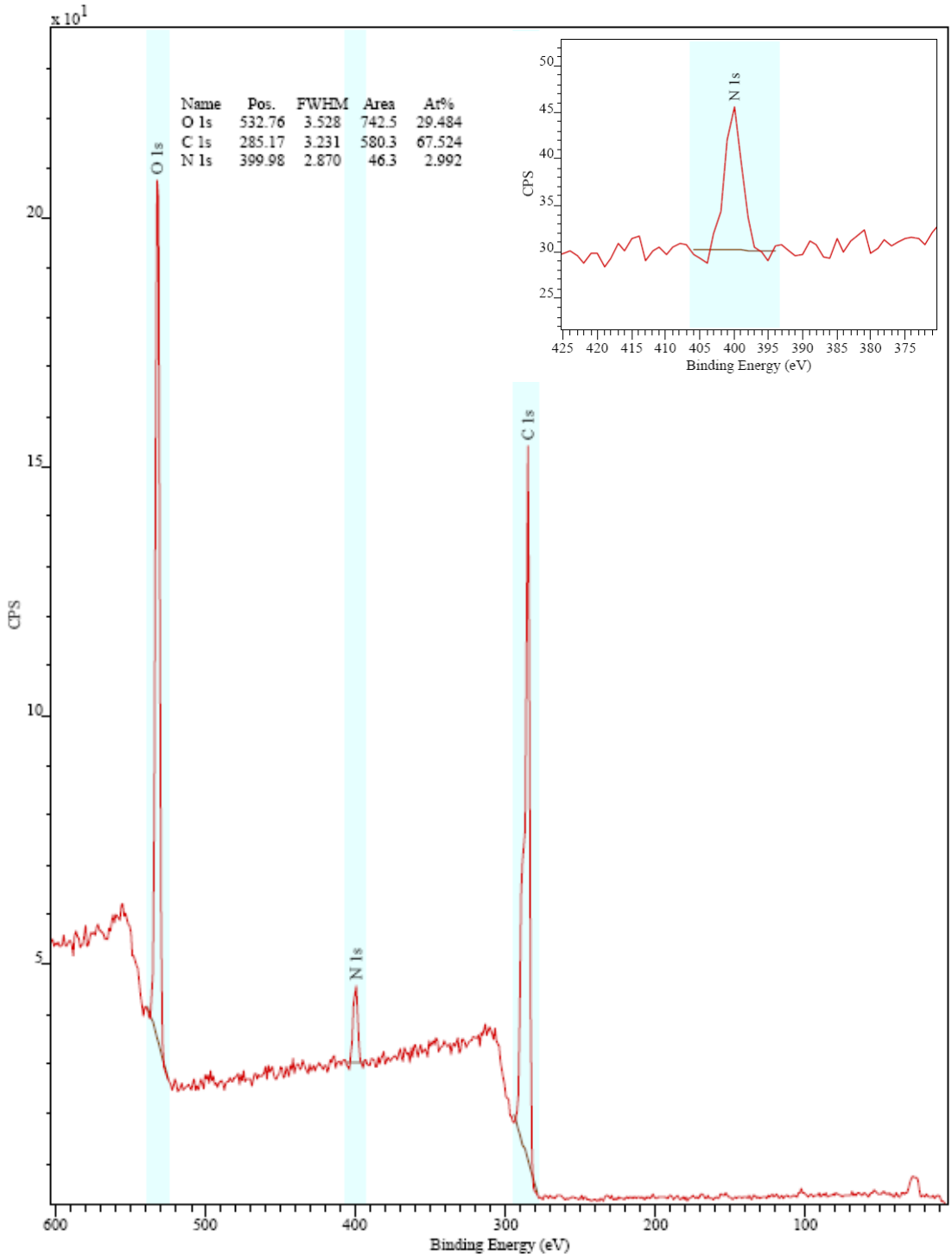


Figure 11 XPS spectrum of plasma-treated polyester with air for 150s at 1.65Torr of pressure.

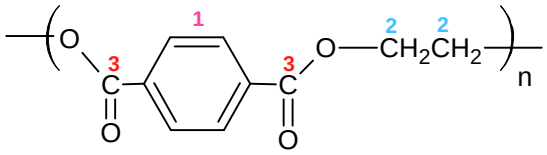


Figure 12 Diagram of the repetitive unit in a polyester chain. PET consists of an aromatic ring, an aliphatic chain, and an ester chain. The structure contains three types of carbon and two types of oxygen that should appear on the XPS analysis *(4)*.

Each type of carbon generates a unique peak on a different level of binding energy as each carbon is bonded to a different component with different electronegativity. In XPS analysis, a photon of energy *hv* bombards the polymer that is being evaluated. The photon is absorbed by an electron from the polymer with a certain binding energy. This electron is then ejected into the vacuum with finite kinetic energy and further analyzed with an electron detector. Consequently the position of the peaks in the spectra depends very much on the components of the bond. For example a carbon-hydrogen bond behaves similarly to a carbon-carbon bond because hydrogen has very low electronegativity (2.2) and therefore does not influence the electronegativity of carbon (2.55), which acts as if it were bonded to another carbon atom. In the case of a carbon-oxygen bond, oxygen (3.44) is more electronegative than carbon (2.55), attracting carbon's electrons and leaving carbon more electropositive. As a result it is more difficult to "extract" an electron from this carbon, requiring more energy. That is the reason the peak related to a carbon atom bonded to an oxygen atom shifts to the left (higher energy level). These phenomena can be observed in the spectra presented in Figure 13, where the peak at 284.7eV corresponds to carbon 1, the peak for carbon 2 appears around 286eV, and that for carbon 3 appears about 288eV *(43)*. Figure 13 shows the spectrum of an untreated PET sample while Figure 14 presents the carbon deconvolution of plasma-treated polyesters under a range of times.

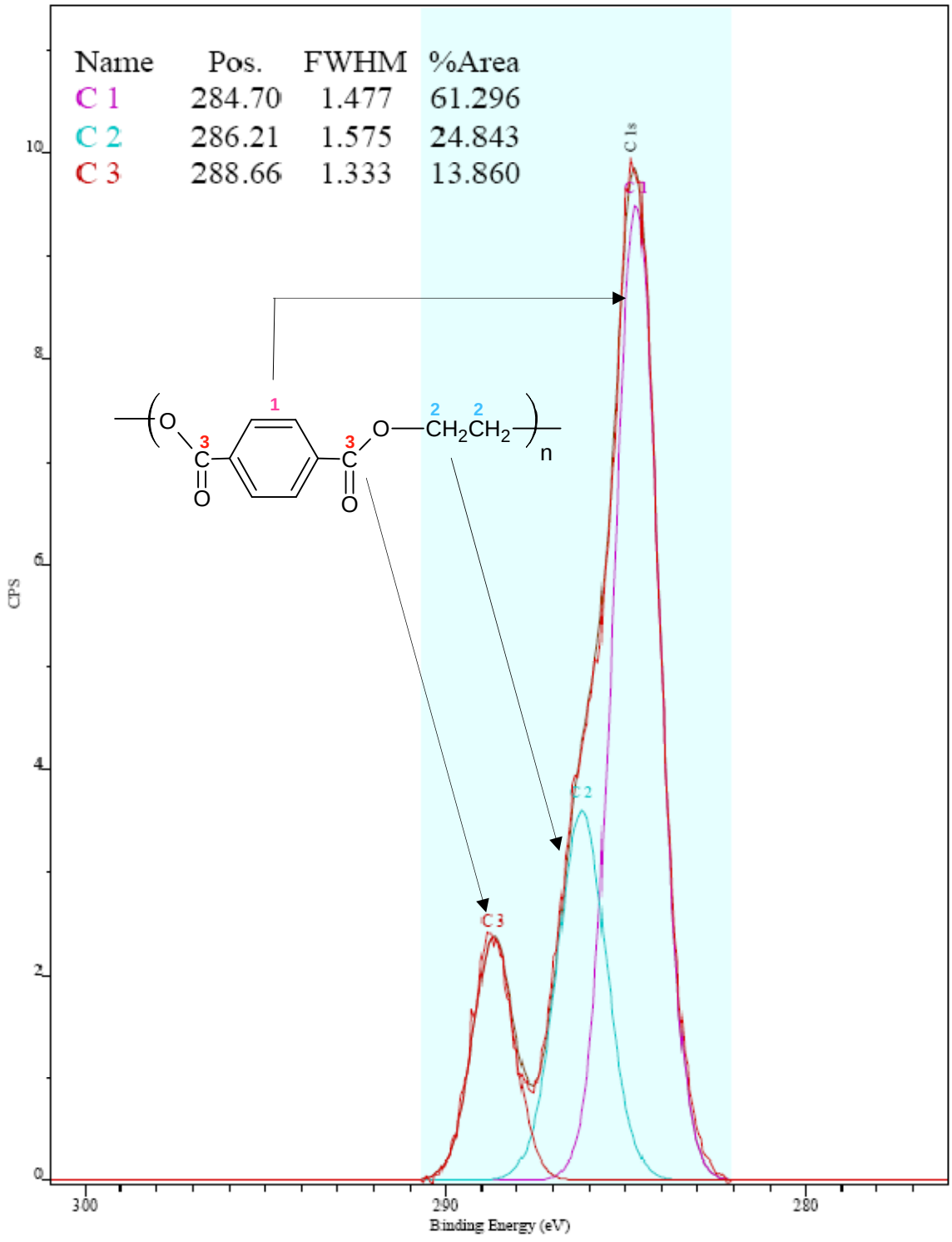


Figure 13 Deconvoluted XPS spectrum of carbon 1s in untreated polyester.

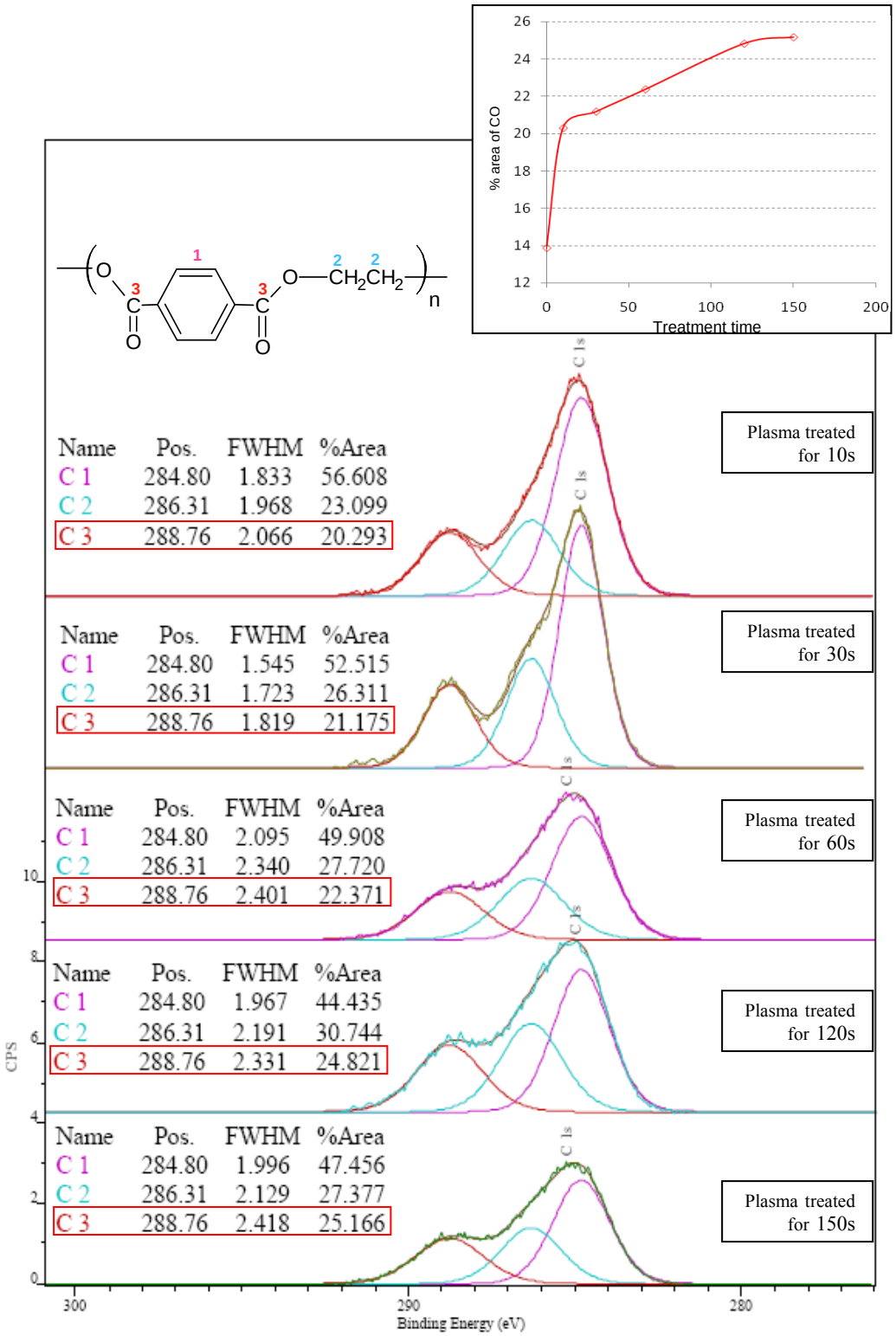


Figure 14 XPS spectra for C1s of plasma treated polyester. It is possible to observe an increase in the area of the peak corresponding to COOH groups (C2) at a binding energy of approximately 288eV when the fabric is treated for longer periods of time. The longer the plasma treatment the more radicals can be created in the PET structure and the more oxygen groups can be introduced.

By means of XPS analysis it is possible to observe the difference between the untreated and treated samples. Untreated polyester is 13.86% carbon number 3. During the plasma treatment the fabric is oxidized. It is possible to observe in the XPS spectra that the percentage of carbon from the COOH group increases from 13.860% in the untreated fabric to 25.166% in the sample treated for 150s. Figure 14 shows an increase in the percentage of COOH groups with increasing treatment time. As a consequence, we believe that the oxygen groups introduced were forming carboxylic groups in the polymer structure.

2.3.2 Hydrophilicity measurements

The plasma-treated fabrics presented at 100% hydrophilicity. Figure 15 shows the water absorption by the untreated and plasma-treated polyester samples.

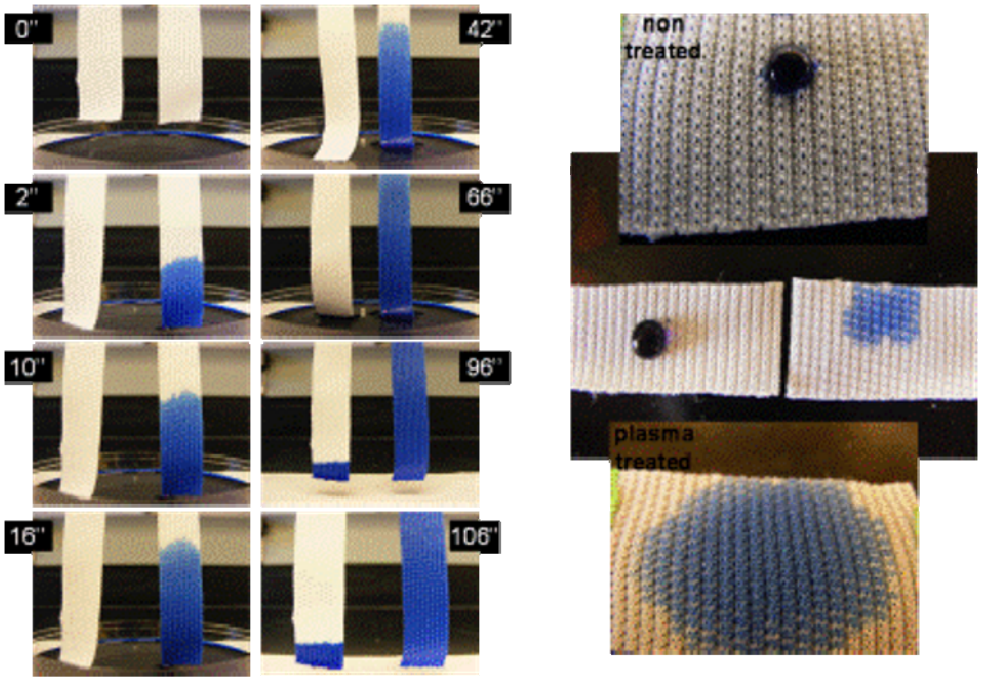


Figure 15 Hydrophilicity tests for treated and untreated polyesters. The fabrics on the left were not treated, while those on the right were plasma-treated with air for 120s. It was possible to observe that the untreated sample absorbed the solution to a limited extent, while the plasma-treated fabric completely absorbed the colored water in less than 2 minutes. These results are an indication that polar reactive groups were created over the PET surface after the plasma treatment.

Figure 16 Results from dyeing processes. A) Dyeing with the disperse dye. No differences were observed between the plasma-treated and untreated fabrics. The dyeing exhibited good fastness as the color remained the same after rinsing. B) Dyeing with the reactive dye. The dyeing of treated and untreated samples showed the same unsatisfactory results before and after rinsing. No color was absorbed by the polyesters. C) Dyeing with the acid dye. The results of dyeing over the treated and untreated PET were not satisfactory and the fabrics presented no color at all after rinsing. However, it is possible to observe that before rinsing some color was deposited over the untreated sample, while the treated PET was still non-colored. The absence of dye over the treated PET could be a result of a repelling phenomenon due to the presence of charges over the fabric surface after the plasma treatment. D) Dyeing with basic dye. The treated and untreated polyester fabrics dyed with basic dyes presented no color after rinsing. However, it is possible to observe a superficial deposition of dye over the treated fabric. This light color could be the result of an attraction between dye and negative charges that remained over the fabric surface after the plasma treatment.

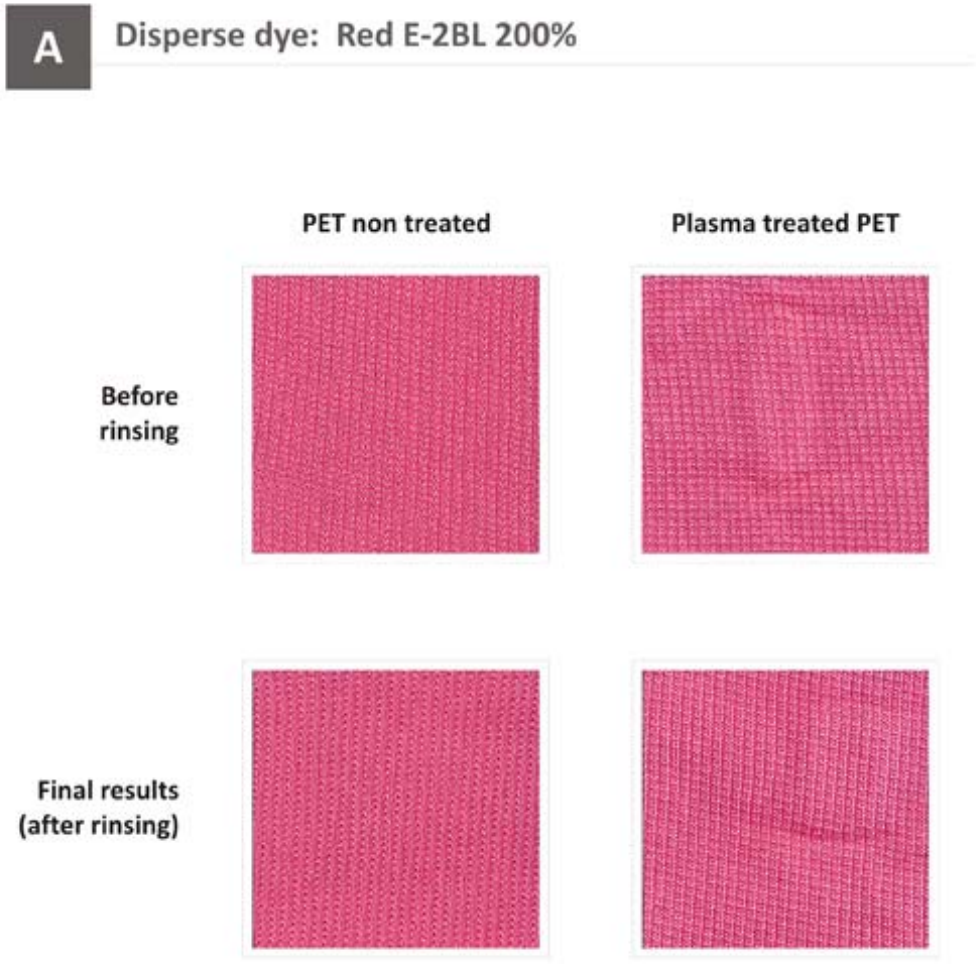

A
Disperse dye: Red E-2BL 200%
PET non treated
Plasma treated PET
Before rinsing
Final results (after rinsing)

Figure 16 (Continued)

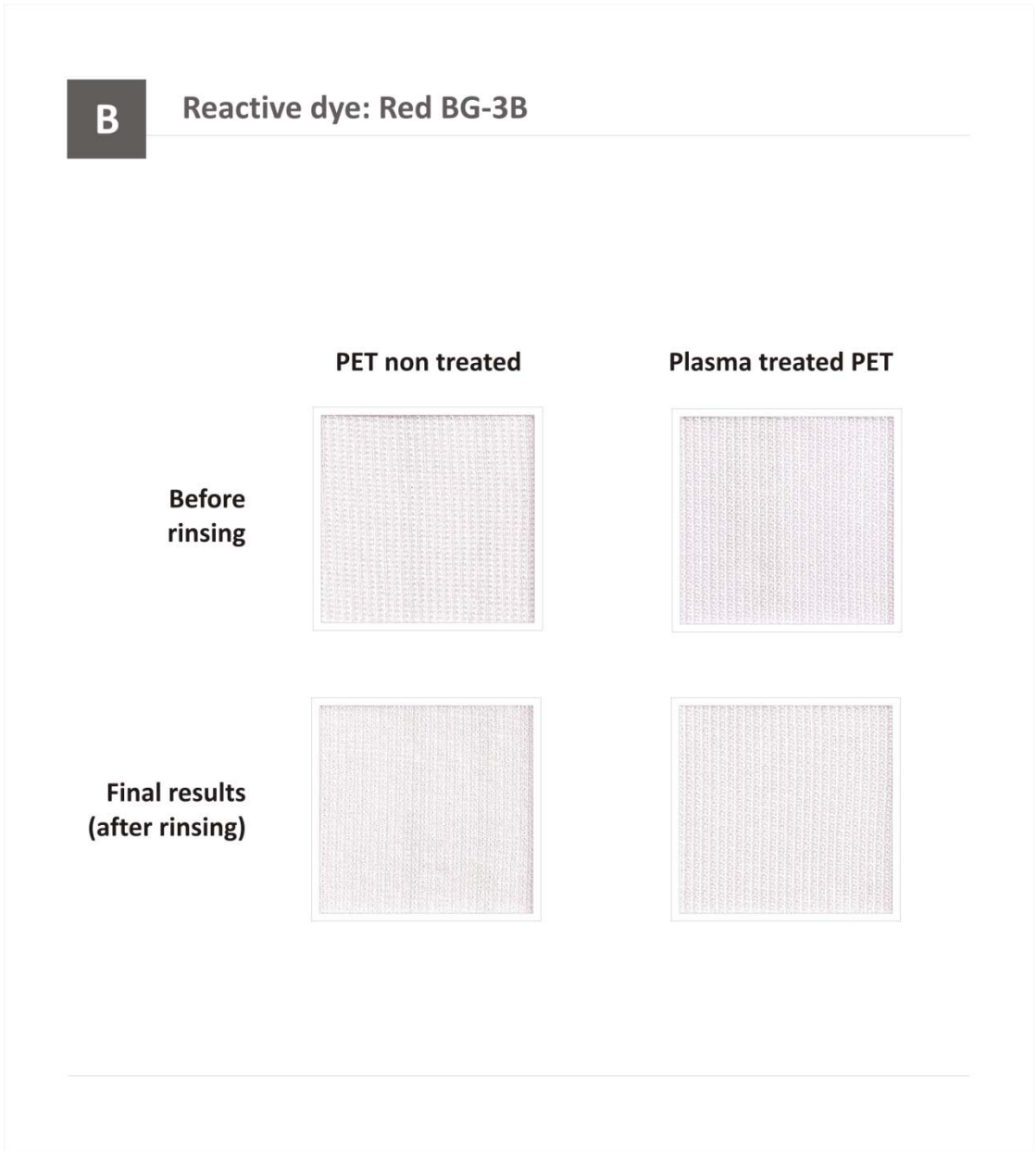


Figure 16 (Continued)

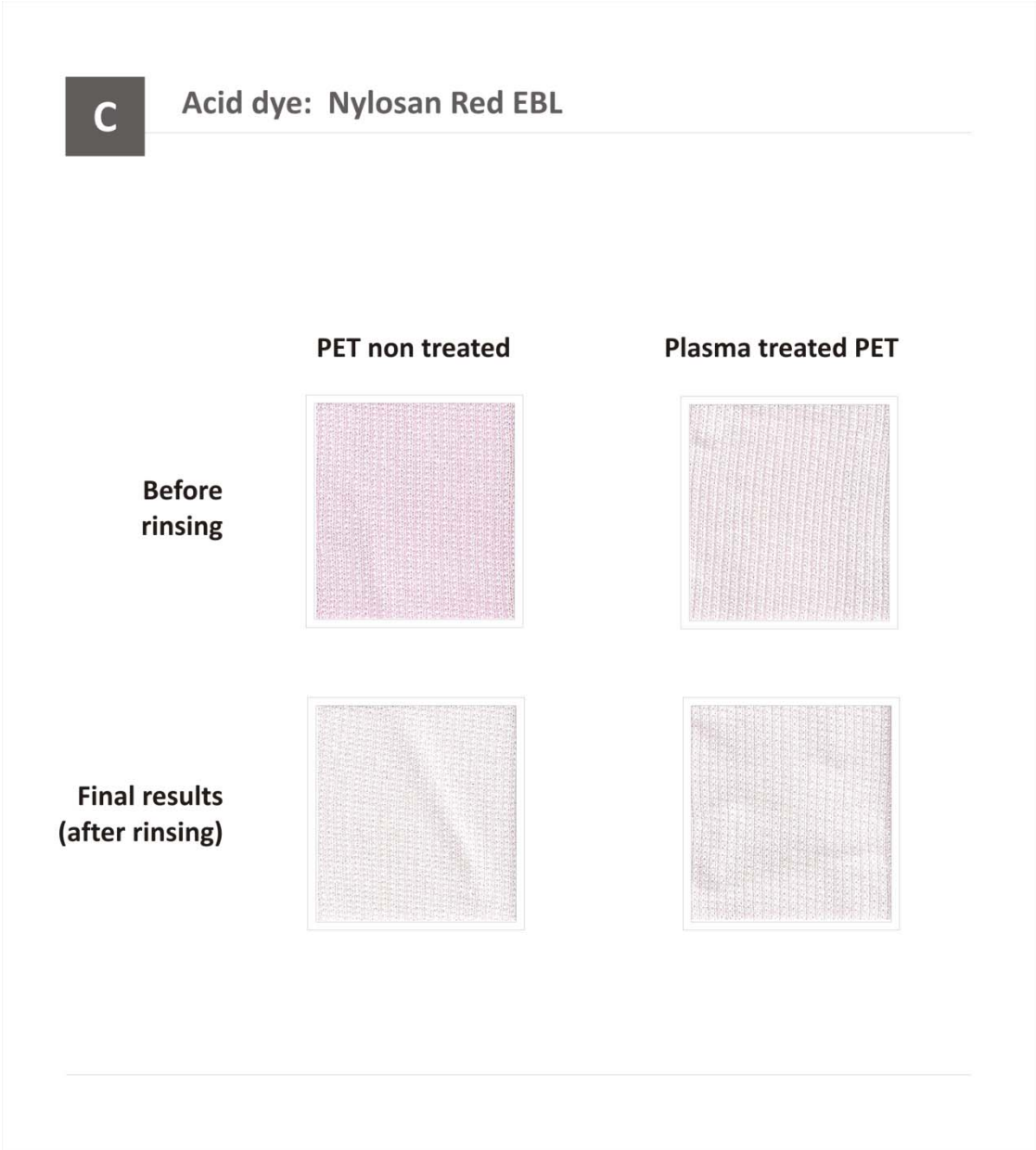
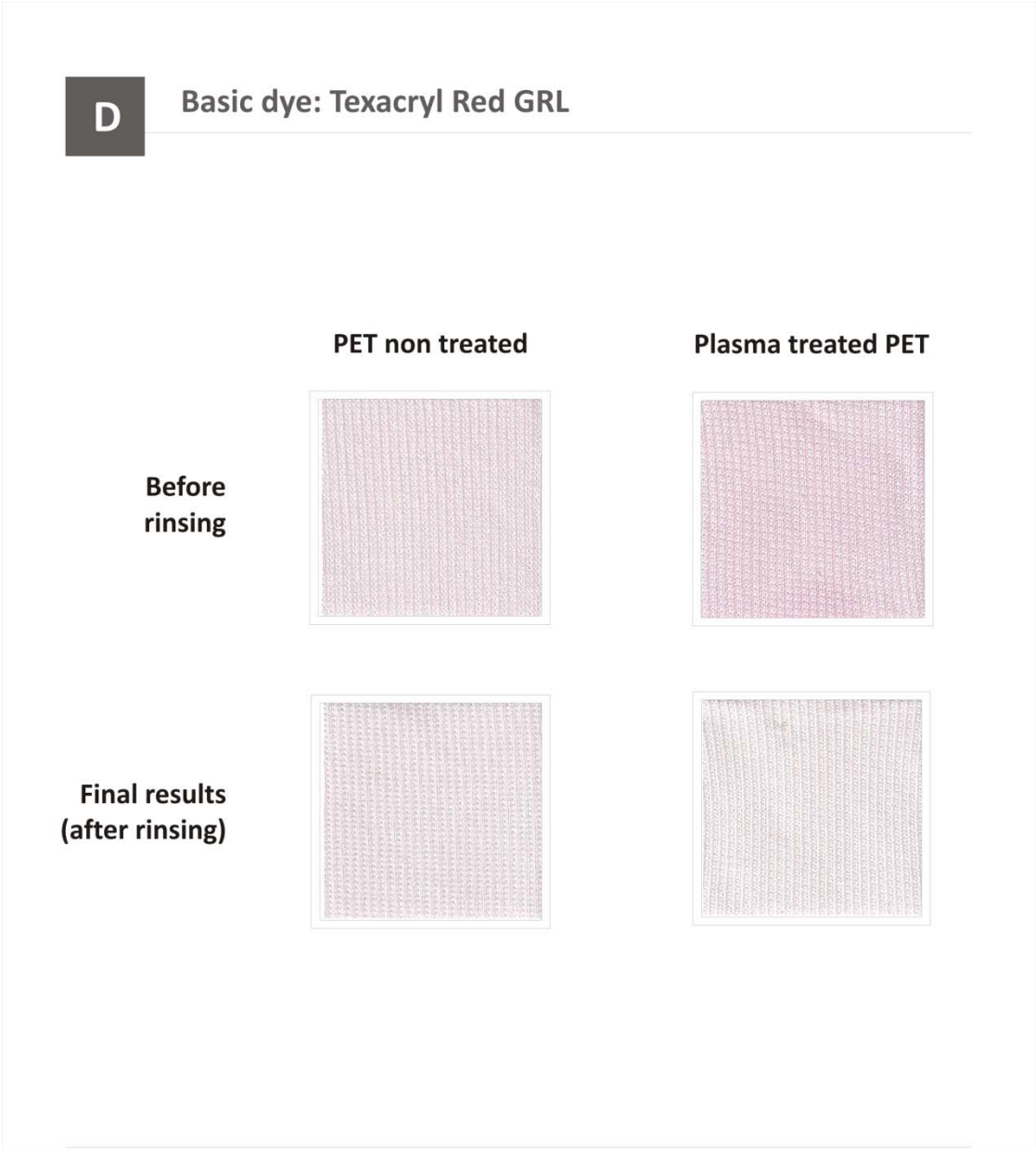


Figure 16 (Continued)



2.3.1 Sample dyeing

Dyeing was used as a way to identify the type of reactive groups created over the polyester surface after plasma treatment. We tested four different classes of dyes: disperse, reactive, acid, and basic.

Reactive dyes are usually employed for dyeing cotton fibers. The reaction occurs between the hydroxyl groups presented on cotton and the reactive ring in the dye *(5, 44)*.

Even though the XPS analysis presented an increase in the peak corresponding to COOH groups in PET, we wanted to make sure the oxygen introduced into the PET structure was from carboxyl and not from hydroxyl groups. We chose to use reactive dyes to indicate OH groups that could have been introduced over the polyester surface during plasma treatment. We believe that if the oxygen shown in the XPS analysis belonged to any hydroxyl groups, the predicted reaction between the modified fabric and the reactive dye should occur.

Acid dyes are commonly used to dye polyamides and protein fibers such as wool, angora, and cashmere. The reaction usually occurs between the amides in the fibers and the anions in the dye molecule. Fastness therefore is usually driven by ionic bonding, Van der Waals forces and hydrogen bonding. XPS analysis showed the presence of an amide group in the polyester fabrics after plasma treatment. We aimed to confirm the presence of these groups by reacting to the modified PET with acid dyes.

Basic dyes are usually applied over acrylic fibers. They consist of an organic cation that combines and stains negatively charged macromolecules. This class of dye could be an indicator of the presence of carboxylic groups in the modified polyester.

Finally we also evaluated the dyeing with disperse dyes, which is the class suitable for polyester. We wanted to evaluate if there was an apparent difference in

color between the plasma-treated and untreated fabric. The results from the dyeing are presented in Figure 16.

The only class of dye that obtained successful results after dyeing and washing was the disperse dye. In addition, no differences were observed between the treated and untreated fabrics *(5)*.

Even though the acid and basic dyeing methods did not succeed, they resulted in some interesting observations, as explained in Figure 17c.

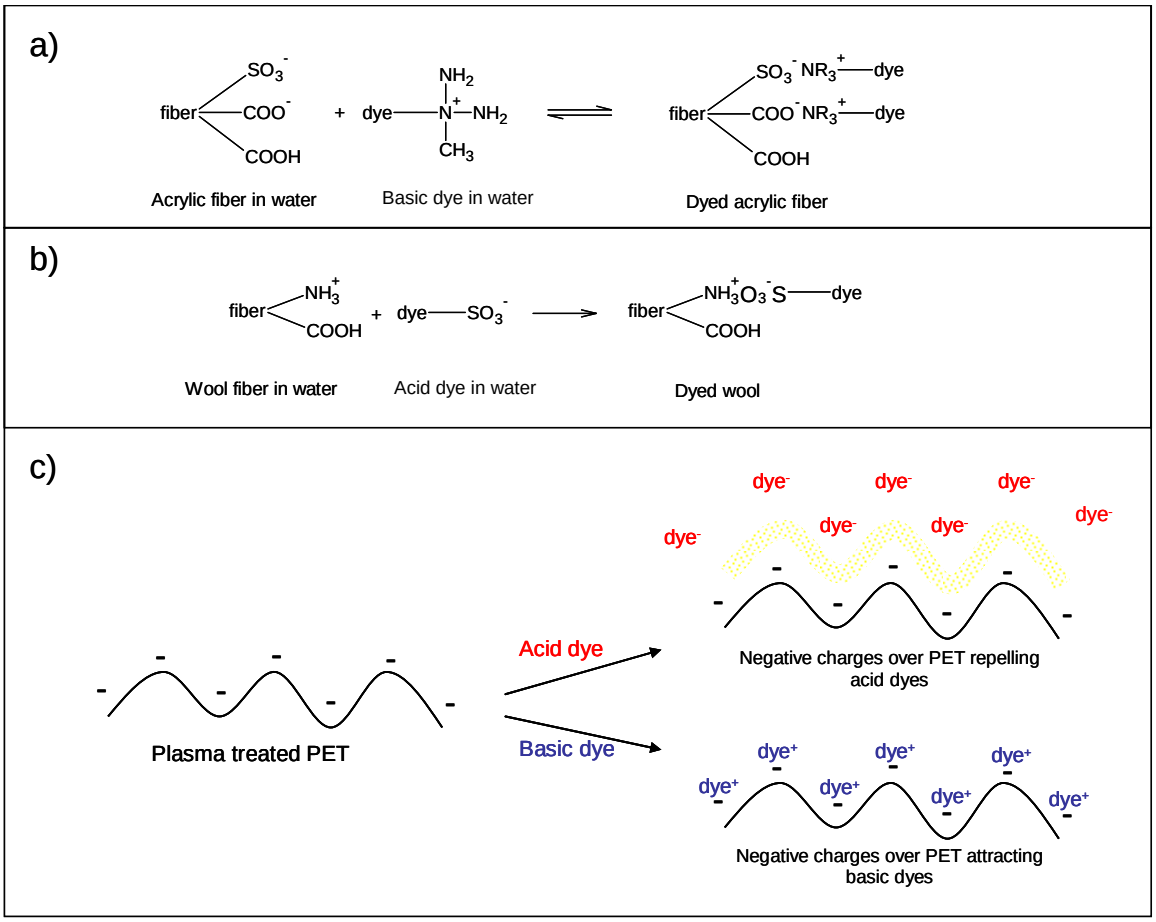


Figure 17 a) Reaction between an acrylic fiber and a basic dye. b) Reaction between wool and an acid dye. c) Reaction between plasma-modified PET and acid/basic dyes. The reaction of wool and acrylic fibers with dyes takes place on the basis of an ionic bond. The negative acrylic fiber in water reacts with the positive basic dye, while the positive wool reacts with the negative acid dye. For our modified polyester, the acid dye was repelled from the fabric, while the basic dye was physically attracted by surface charges and was deposited over the fabric surface. This could be evidence of the presence of negative charges of the plasma-treated polyester.

In the dyeing process using acid dyes the treated fabric repelled the dye, while the untreated fabric presented a light deposition of the acid dye over its surface. On the other hand, in the process using the basic dye, the plasma-treated polyester attracted more dye molecules than the untreated fabric did. This could be evidence that polyester becomes negatively charged after air plasma treatment. Another hypothesis was that the negative charges over the modified polyester surface resulted from ionization of carboxylic groups that were created over the treated fabric surface. XPS showed an increase in the peak corresponding to the COOH groups in the PET structure. It is unlikely, however, that the created carboxylic groups would be able to repel or attract the acid and basic dyes. The dyeing of fibers with basic dyes is possible due to an ionic bond that is formed between the carboxylic groups from the fiber and the dye. This ionic bond is what makes the dye fasten to the fiber. In our case the dyeing exhibited no fastness to the fiber. After washing all color, the basic dyeing was gone. Such weak fastness indicates that no reaction occurs between the carboxylic groups and the basic dye. Therefore it is possible to confirm that the repelling/attracting phenomena observed during dyeing with acid and basic dyes was a result of negative charges deposited on the polyester surface after plasma treatment. There was no chemical bond between the dye and the fibers, possibly because the amount of COOH groups evidenced in the XPS analysis was very small and could not react to the fiber up to the point at which the color would become noticeable.

2.4 Conclusions

Low-pressure air plasma treatment has shown a capacity to impart hydrophilicity to polyester fabrics. XPS analysis revealed the introduction of oxygen and nitrogen groups on the polyester surface. Based on findings in the literature and the position of the peak in the XPS spectra, the introduced nitrogen groups are amides.

Dyeing experiments were carried out in order to evaluate the components introduced over the polyester surface by type. Four classes of dyes were tested: disperse, acid, reactive, and basic dyes. No difference was observed between the treated and untreated fabrics after dyeing. We believe that insufficient amounts of the reactive groups were introduced over the surface.

Air plasma treatment introduced polar groups over the polyester surface, imparting wettability to the fiber. These groups were not able, however, to functionalize the fabric in order to react with the various types of dyes. We believe that one possible option for increasing the reactivity of the fiber is the use of pure gases in the plasma process. Pure gases could direct more of the reaction in the direction we want because we can control more precisely what is being formed in the plasma. For example, the use of ammonia gas instead of air could add more nitrogen groups over the surface of the fabric than is possible using air containing a mixture of gases. We also believe that the use of inert gases in the process would increase the reactivity of the treatment. Inert gases do not expend energy in reacting with other particles, so they can transfer more energy in collisions and also help in maintaining the plasma. We therefore propose as a next step the use of inert gases such as argon or helium in the plasma process.

CHAPTER 3: SURFACE MODIFICATIONS OF PET FABRICS WITH LOW PRESSURE ARGON PLASMA.

3.1 Introduction

The goal of this project was to improve the polyester dyeing process by utilizing reactive dyes. Reactive dyes are well known for good color quality and fastness results *(5, 6, 45)*. Moreover, the dyeing process with reactive dyes is carried out under ambient or slightly warm temperatures.

We first treated the PET fabrics with argon plasma in order to create radicals in the polymer structure. Second, the fabrics were oxidized by exposure to ambient air. The oxidation resulted in the formation of oxygen reactive groups over the PET surface that were able to react with the dye.

3.2 Experimental

3.2.1 Materials and equipment

Fabrics of 100% polyester (0.014g/cm2) containing 76% yarn 165/72 with 1000 twists and 24% yarn 78/24 (unifi bright) from Fibra S/A - Brazil were employed. The fabrics were previously purified with 2,0g/L of detergent (Goldpal VP from Golden Quimica - Brazil) and 0,5g/L of acetic acid (from Labsynth) for 30 minutes at 80°C.

Argon gas was acquired from Airgas. PET fabrics were dyed with Color Index (CI) reactive orange 4 from ICI Chemicals and CI reactive blue from Hoechst. Sodium

chloride and sodium carbonate anhydrous were obtained from Panreac Quimica SA. – Spain. Sandopan DTC soap was bought from Clariant Iberica.

The reactor employed for the plasma treatment was an IPE 1000 Plasma Enhanced Chemical Vapor Deposition with RF with 50kHz available at the Cornell Nanoscale Science & Technology Facility (CNF) at Cornell University. Figure 18 shows a picture of the reactor and a scheme of the experimental setup.

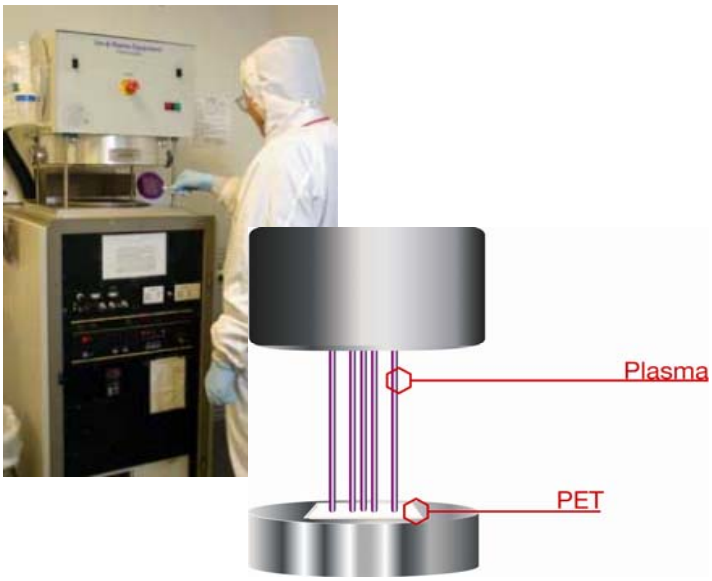


Figure 18 IPE 1000 Plasma Enhanced Chemical Vapor Deposition System available at the Cornell Nanoscale Science & Technology Facility (CNF) at Cornell University.

3.2.2 Plasma treatment and analysis

The PET fabric was cut into 7cm x 12cm pieces. The pieces were further treated under a flow of 21.3sccm of argon plasma at a 180w power level. The duration, pressure, and temperature were varied according to Figure 19.

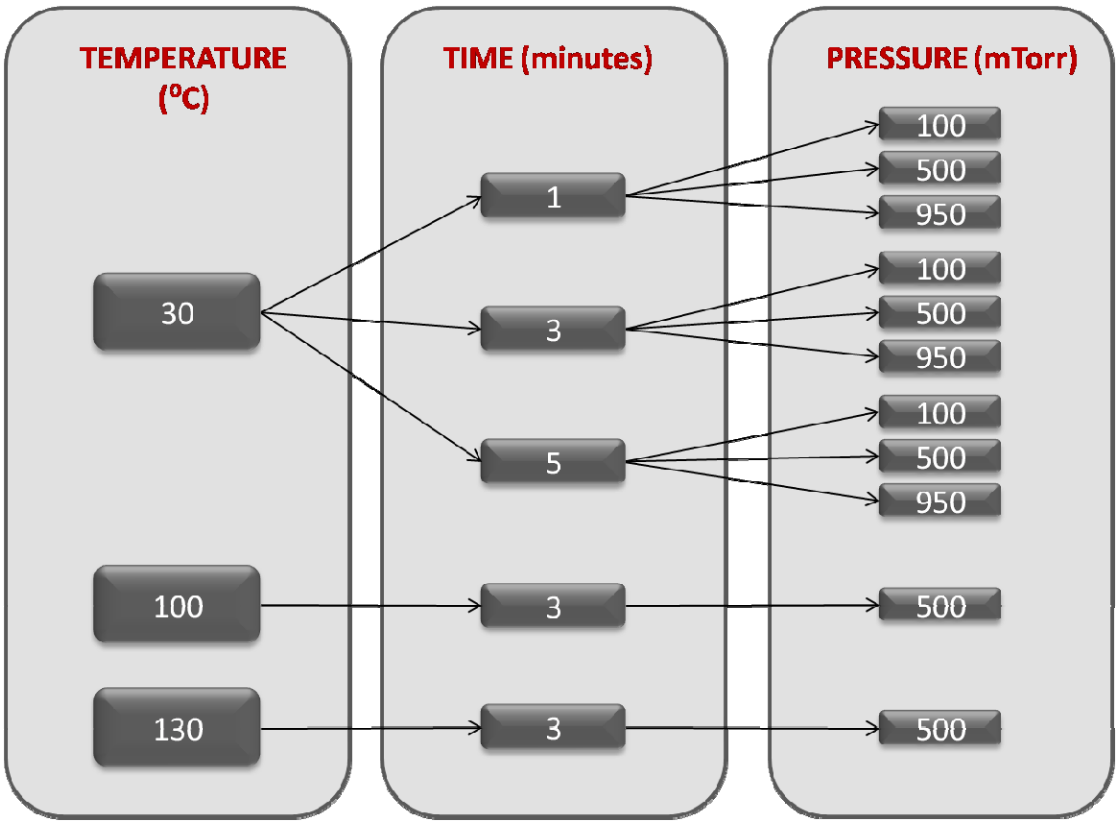


Figure 19 Schematic for the plasma experiments. At a temperature of 30°C three treatment durations (1, 3, and 5 min) were evaluated under three pressures (100, 500, and 950mTorr). At temperatures of 100°C and 130°C, the treatments were realized at 500mTorr of pressure for 3 minutes.

3.2.3 X-ray Photoelectron Spectroscopy (XPS)

XPS analyses were obtained on an SSX-100 system equipped with a hemispherical analyzer and a monochromatic Al Kα x-ray source with 1486.66eV of energy. The analyzer pass energy was 150V for survey scans and 50V for high-resolution scans. Photoemission electrons were collected from the sample at a 55-degree emission angle. The beam spot was 1mm in diameter, incident on the sample at 55 degrees from surface normal, which resulted in an ellipse of about 1mm x 2mm. The operating pressure was around $2x10^{-9}$Torr.

3.2.4 Hydrophilicity tests

Two pieces of fabric (plasma-treated and untreated) measuring 1.5cm x 12cm were suspended over a plate with blue dye in solution. The solution contained 1g/L of Methylene blue dye (from Acros) for visual evaluation of water absorption by the fabric. The two pieces of textile were placed vertically in contact with the solution absorbing it. The absorption rate was assessed using high-speed photography.

3.2.5 Thermosetting

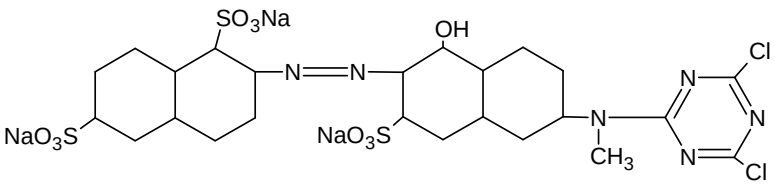
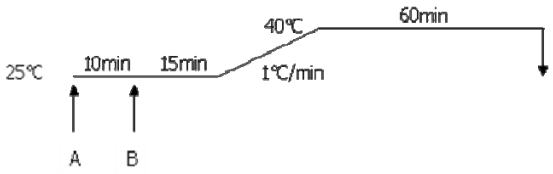
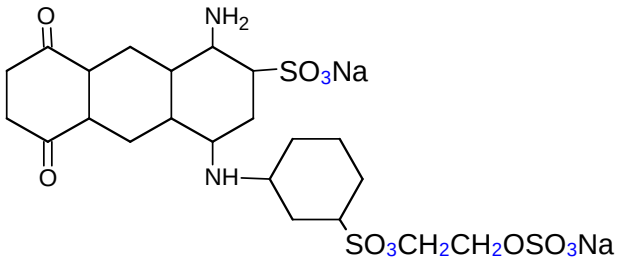
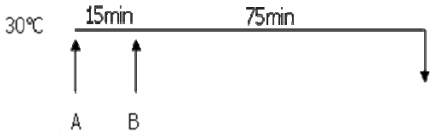
Thermosetting is a fabric process common to most thermoplastic fibers, aimed at obtaining dimensional stability of the fabric for further processing such as dyeing and finishing. The process consists in heating the fabric above its glass transition temperature but below the melting temperature, while applying tension. The dimensional stability is the result of a reorganization and realignment of the molecular chains *(46, 47)*.

Thermosetting was realized in a fixotest (model 7501 from Original Hanau - Germany) at 220°C for 30 seconds for each sample.

3.2.6 Dyeing procedures

The dyeing procedure is explained in Table 2.

Table 3: Dyeing processes with reactive dyes

<table>
<tr><td>Dye
CI reactive orange 4</td><td colspan="2">  </td></tr>
<tr><td colspan="2">Dyeing process</td><td>Products</td></tr>
<tr><td colspan="2">  </td><td>A: 80g/L NaCl
5g/L Na2CO3
NaOH until pH 12
B: 1% owf dye</td></tr>
<tr><td>Dye
CI reactive blue 19</td><td colspan="2">  </td></tr>
<tr><td colspan="2">Dyeing process</td><td>Products</td></tr>
<tr><td colspan="2">  </td><td>A: 35g/L NaCl
NaOH until pH 12
B: 1% owf dye</td></tr>
</table>

For the dyeing process with CI reactive Orange 4 an aqueous solution with 1% over weight of fiber of the dye and 35g/l of sodium chloride was used. Sodium

hydroxide 36°Be was employed for pH adjustment. Two pHs were evaluated: The first set of experiments was realized under a pH of 12 and the second set was done at a pH of 10. The bath ratio was 1g of fabric per each 100mL of bath (1:100) and the process was carried out in a glass beaker over a heater and stirrer plate. The temperature was kept at 30°C. First the treated and untreated fabrics were introduced in the solution with NaCl and NaOH and kept there for fifteen minutes. This first step was taken to ensure ionization of the OH groups from the treated PET surface. Following this step, the diluted dye was introduced and the fabric in solution was stirred constantly for 75 minutes.

In the reactive Orange 4, a dichlorotriazinyl type, the reactive ring is bonded to an amine group from the chromophore, and the whole molecule reacts with the hydroxyl group of cellulose. The reaction is shown in Figure 20.

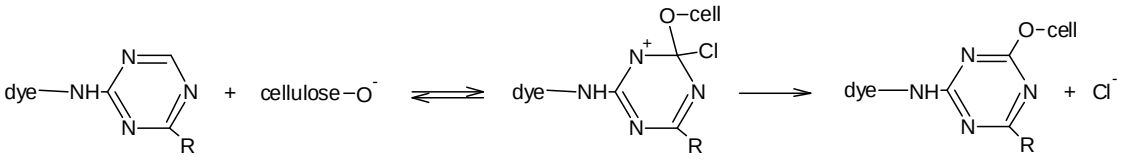


Figure 20 Reaction between a dichlorotriazinyl dye and cellulose *(5-7)*

This reaction is possible due to the high electronegativity of nitrogen, which induces an electronic attack in its carbon neighbor that allows it to react with other groups. This reaction is employed to produce cellulose esters *(5)*.

For the dyeing process with CI reactive blue 19, a vinyl sulphone type, an aqueous solution with 1% over weight of fiber of the dye, 80g/l of Sodium chloride and 5g/l of Sodium bicarbonate was used. Sodium hydroxide 36°Be was employed for pH adjustment. The process was realized in a glass beaker with a bath ratio of 1:100. The beaker was kept over a heater and stirrer plate for constant stirring. The initial

temperature was 25°C. In order to assure ionization of the hydroxyl groups from the plasma-treated PET, both samples (treated and untreated fabrics) were first kept in the solution with NaCl and NaOH for fifteen minutes. Second, diluted dye was introduced and the fabric in solution was stirred constantly for 15 minutes. The bath was warmed to 40°C at a rate of approximately 1°C/min and then stirred constantly for 60 minutes. The reaction between the fiber and a vinyl suplhone dye in the simplest case is shown in Figure 21.

$$\text{dye} - SO_2 - CH = CH_2 + HO - \text{cell} \xrightarrow{\text{alkali}} \text{dye} - SO_2 - CH_2CH_2 - O - \text{cell}$$

Figure 21 Reaction between a vinyl sulphone dye and cellulose. *(8)*

Dyed fabrics were washed for 15 minutes at 100°C with a water solution containing 2g/L of the detergent Sandopan DTC and 2g/l of sodium carbonate (CO_3Na_2) to remove any residual dye from the fiber surface.

3.2.7 Color measurements

The color of dyed fabrics was measured with a Macbeth color-eye® 7000 spectrophotometer. The calculation of the difference in color was carried out using the software Super Color Dye version 5.0 according to the normative ISO 105-J03: 1995. The spectrophotometer measurements were based on the so-called *CIELAB* system, which derives from two colorimetric systems: the stimuli (*CIE*) and the sensation-based (*HSB*). Recommended by the *Commission International de l'Eclairage (CIE)*, the *CIELAB* is considered the universal standard system for color evaluation *(48)*.

The calculation provides a numerical value (ΔE_{cmc}) that describes an ellipse, with axes represented by lightness (lS_l), chroma (cS_c) and hue (S_H), in the center of

which the sample reference is located. The equation used to calculate ΔE_{cmc} is the following:

$$\Delta E_{cmc} = [\ (DL/\ lS_l)^2 + (Dc/\ cS_c)^2 + (DH/\ S_H)^2]^{1/2} \quad [8]$$

where DL, Dc and DH are the differences in lightness, chroma and hue between sample and reference, respectively, and lS_l, cS_c, S_H are the axes of the ellipse. In the analysis, the axes representing chroma and hue are the red-green axis and blue-yellow axis.

The analysis was carried out with blue light (D65) at 10° and l:c was 1:1.

3.2.8 Atomic Force Microscopy

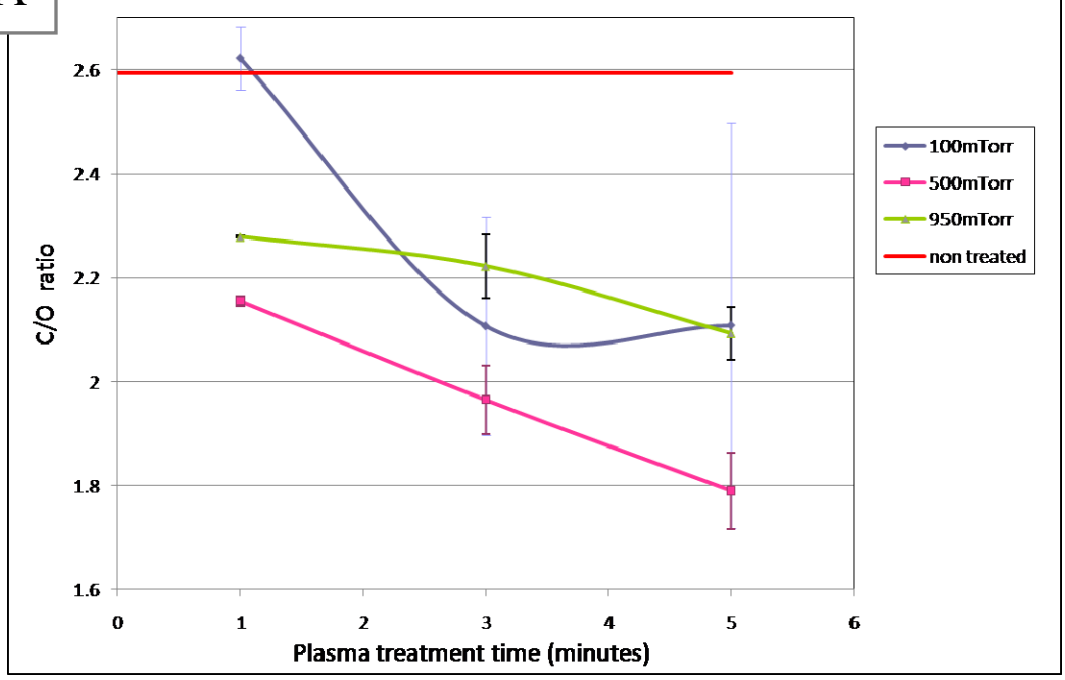
Topographical studies of the fabric surface were carried out using an NTEGRA Atomic Force Microscope from NTMDT. A microfabricated rectangular silicon cantilever with a theoretical spring constant $k = 0.2^{-1}$ N m^{-1} and a resonance frequency of approximately 75 kHz was employed to image the treated and untreated polyester fibers. Squares of 100µm x 100µm were scanned under constant applied force conditions. Due to the irregularity of the fabric, tapping mode in air was preferred over contact mode. Software Nova 1443 was used for the image processing and data analysis.

3.2.9 Field Scanning Electron Microscopy

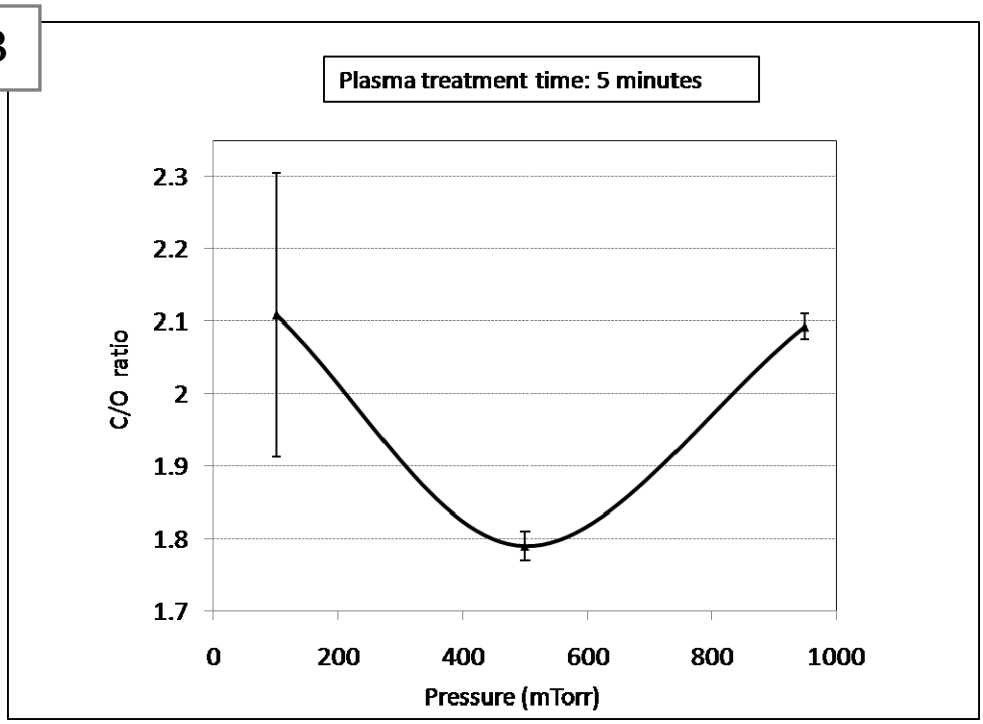
Scanning electron microscopy imaging was performed using a Hitachi 4500 cold-field emission SEM at an accelerating voltage of 1kV to avoid charging and less current to avoid melting of the polymer.

Figure 22 C/O ratios on the fiber as a function of pressure and time after argon plasma exposure. The smallest C/O ratios were obtained at 500mTorr of pressure. A large error can be seen from the results obtained with the 100mTorr treatment compared with the results obtained under other pressures. During the treatment at 100mTorr it was possible to observe a rapidly time-varying discharge in the sheath layer very close to the fabric, which may account for the large error seen in the graphic. The error means the experiments were not reproducible. At a pressure of 950mTorr the plasma was stable, which also resulted in a uniform introduction of oxygen groups. However, at 500mTorr the treatment was more effective as a result of having oxidized more of the fiber.

A


2.6
2.4
2.2
2
1.8
1.6
C/O ratio
0
1
2
3
4
5
6
Plasma treatment time (minutes)
100mTorr
500mTorr
950mTorr
non treated

B


Plasma treatment time: 5 minutes
2.3
2.2
2.1
2
1.9
1.8
1.7
C/O ratio
0
200
400
600
800
1000
Pressure (mTorr)

3.3 Results and Discussion

3.3.1 Surface characterization by XPS

Chemical modifications of the specimen's surface after argon plasma treatment followed by exposure to air were analyzed with X-ray photoelectron spectroscopy. Figure 22 shows the results obtained for PET fabrics treated under various pressures and durations. All experiments were conducted at 180W of power, at a temperature of 30°C and a gas flow of 21.3sccm, and repeated 3 times.

It is well known that plasma treatment with inert gases causes ablation and formation of free radicals over polymers *(49)*. The oxygen introduced into the PET structure was the result of air exposure after argon plasma treatment *(34, 50)*. The treatment at 100mTorr of pressure did not yield the best results due to the instability of the plasma in the sheath over the fabric. As observed in the XPS analysis, this instability yielded non-uniform results in the introduction of oxygen in the polyester chain. At 500mTorr and 950mTorr of pressure, the plasma was stable and yielded more uniform results. The maximum oxygen introduction, C/O = 1.69, occurred at 500mTorr with a stable plasma after a treatment of 5 minutes with argon. A hypothesis for the best results at 500mTorr is presented below.

Considering that our plasma is weakly ionized ($n=10^{11}cm^{-3}$), we calculated and compared the characteristic ion and electron plasma frequencies with the frequency of our plasma system, which is 50 kHz.

The electron frequency:

$$f_{pe} = \omega_{pe}/2\Pi \qquad [9]$$

where

$$\omega_{pe} = (e^2 n_e /\varepsilon_o m_e)^{1/2} \qquad [10]$$

The ion frequency:

$$f_{pi} = \omega_{pi}/2\Pi \quad [10]$$

where

$$\omega_{pi} = (e^2 n_i/\varepsilon_o m_i)^{1/2} \quad [12]$$

The results obtained were:

$$f_{pe} (\sim 2.8M\ Hz) > f_{pi} (\sim 66kHz) > RF\ (50kHz) \quad [13]$$

Both the ion and electron frequencies were higher than the RF used, which allow us to conclude that both ions and electrons were responsive to the RF electric field in the plasma *(51)*. We believe, however, that ions were not as efficacious as electrons during the treatment, the two main reasons for which, we are able to conclude, were the particle velocity and energy transfer capacity.

At the boundary of the sheath, the velocity of electrons is given by the thermal velocity $v_{th} = (kT_e/m_e)^{1/2}$ and the velocity of the ions is given by the Bohm velocity = $(kT_e/m_i)^{1/2}$, where T_e is the electron temperature and k is the Boltzman constant *(51)*. The ions mass is 1836A times larger than the electron mass, where A is the mass of the ion relative to a proton, causing the ions to be slower than the electrons by a factor of $(1836)^{1/2}$ times. Because of their higher velocity, the flux of electrons will be higher at the boundary of the sheath over the fabric, resulting in a greater number of electrons than ions entering the sheath. Therefore more electrons than ions will be accelerated to the PET surface during a full RF cycle.

The second reason that electrons are more active than ions is related to their capacity to transfer energy during collisions. The voltage that accelerates electrons and ions across the sheath is approximately constant, varying only in sign (positive or negative). Thus ions and electrons that accelerate across the sheath and reach the fabric will have about the same energy. However, because of the difference in their respective weights, electrons are more effective at transferring energy to the electrons involved in chemical bonds in the polymer modifying the surface of the fabric *(13)*.

As a consequence, the electrons are thought to be mainly responsible for the ongoing reactions of the fabric in the plasma. Thus, we should focus on the electrons in the plasma to explain why 500mTorr was the optimum pressure for the treatment. According to findings in the literature, the lower the pressure in a plasma treatment is, the higher is the temperature of the electrons *(10)*. At our working pressures it is possible to analyze the plasma with a Maxwellian distribution and the mean energy can be referred to as temperature *(10)*. Therefore at lower pressures electrons are less collisional and more energetic and the plasma treatment is more effective than with higher pressures. That is why the results for a working pressure of 500mTorr were better than for a pressure of 950mTorr.

We also evaluated the influence of temperature in the plasma treatment. The results are presented in Figure 23.

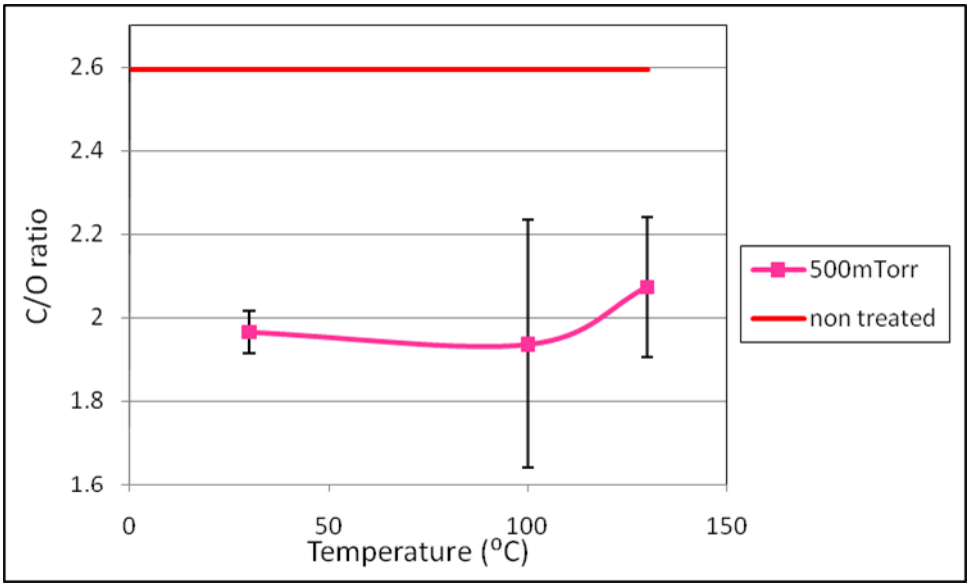


Figure 23 Resulting C/O ratios under varying pressures and temperatures. The P and T combination that gave the best results were 500mTorr and at 30˚C. It is possible to observe not only a maxim amount of oxygen under this condition but also the minimum error, which accounts for greater reproducibility and uniformity.

The trend observed when varying the plasma temperature is in agreement with results previously reported in the literature *(10)*. Due to the high heat sensitivity of polymers, non-thermal plasma processing is the most suitable process to use when treating polymers, due to their high heat sensibility. Cold processes are the best to use for imparting modifications in the polymer without destroying or degrading the fabric.

The stability of the plasma treatment with time (aging) was also evaluated. The conditions of plasma treatment for this evaluation were 500mTorr, 180W, argon flow of 21.3sccm, 30°C, under different periods of time: 1, 3, and 5 minutes. The changes in the C/O ratios due to the ageing process are shown in Figure 24.

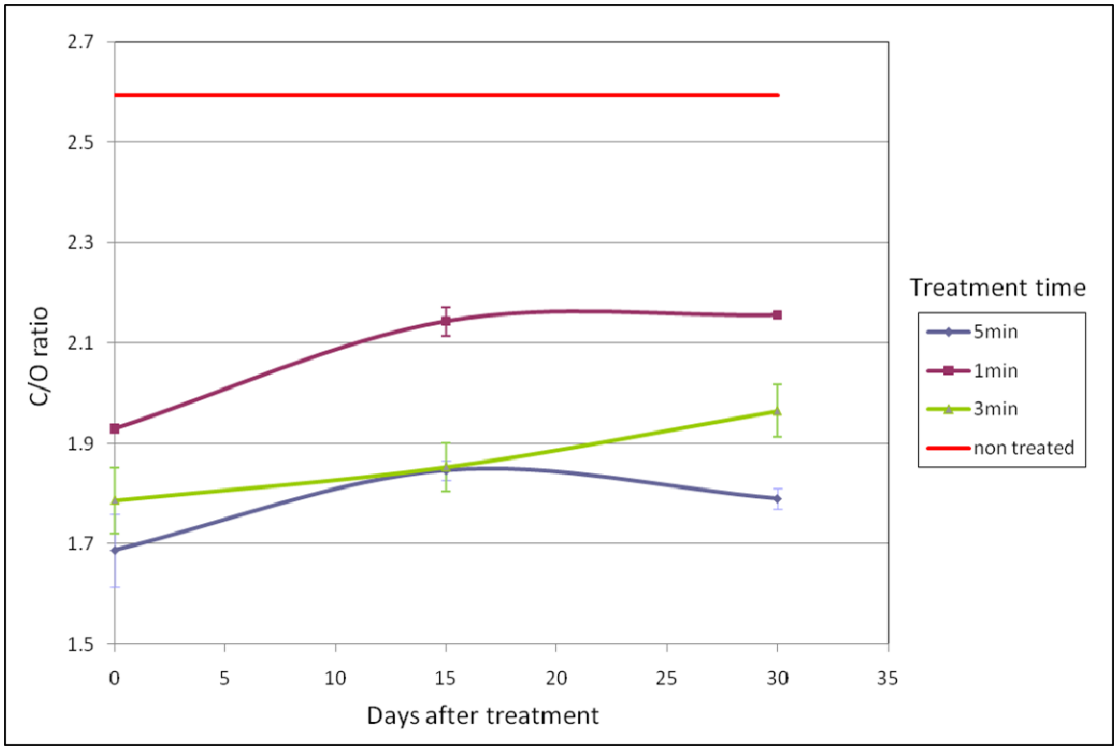


Figure 24 Effect of the aging process on the C/O ratio of the fabric. The treatment was carried out under three different time periods: 1, 3, and 5 minutes. The C/O ratios were evaluated on the same day, 15 days later, and 30 days after the plasma treatment. These ratios were compared with that of an untreated sample. Even though it was possible to observe an increase in the amount of carbon (from 1.8 on the same day to 2.0 after 30 days), the fabric did not return to its original (untreated) state, in which the C/O ratio was 2.6.

The aging process results from the molecular mobility in the polymer chain *(21)*. In a polymer composed by amorphous and crystalline regions, chain mobility occurs mainly in the amorphous zone. The bigger is the amorphous zone in a polymer, the higher is the probability that this polymer will undergo ongoing aging. Our hypothesis for the low aging observed with XPS analysis is based on the high crystallinity of polyester fibers, in which the small amorphous zone in polyester fibers slows down chain mobility and retards ageing.

Quantitative information on oxygen implantation on the polymer surface as a consequence of argon plasma treatment followed by air exposure was inferred from the ratios of carbon to oxygen in the polyester molecule. Our molecular structure hypotheses are presented in Figure 25.

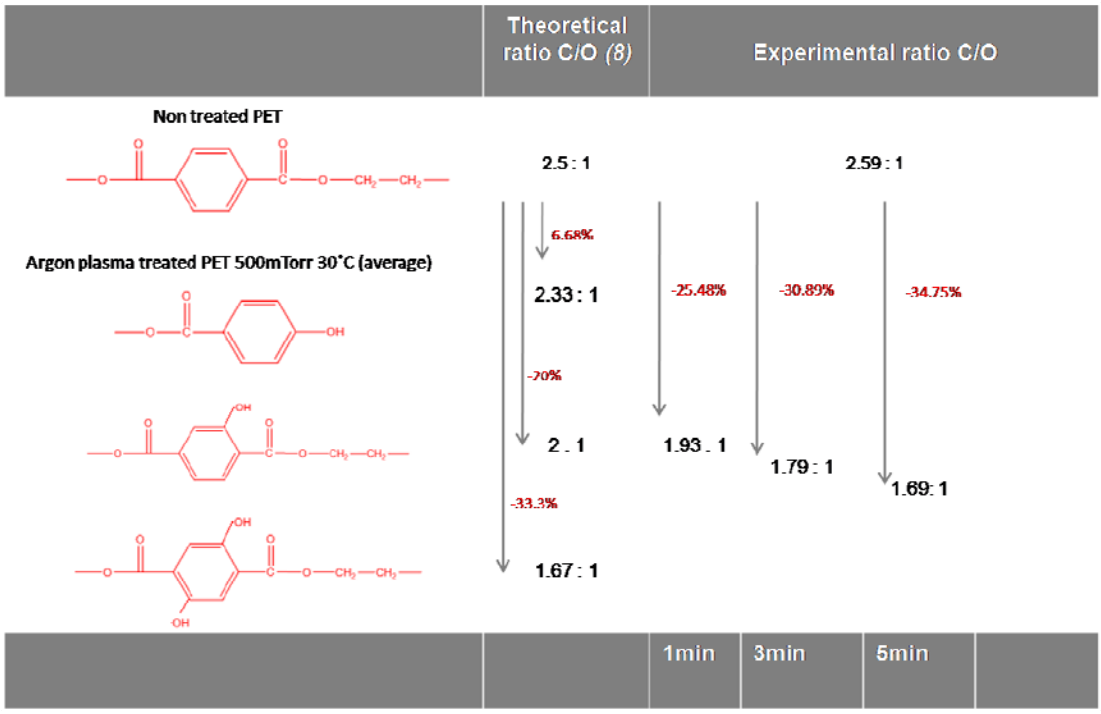


Figure 25 Proposed PET structures formed after argon plasma treatment followed by air exposure. The structures were proposed based on a comparison between the carbon/oxygen ratios of our samples evaluated with XPS with the theoretical values of the proposed PET structures. The percentage numbers in red correspond to the reduction of C/O ratios after plasma treatment. The experimental ratios presented an error incidence of less than 10%.

According to Inagaki *et al.* PET modification is possible due to the formation of a stable radical on the aromatic ring *(34, 50)*. Upon exposure to air, this radical reacts with oxygen, resulting in the formation of a hydroxyl group bonded to the ring. We believe that the formation of one single hydroxyl group in the polyester molecule is the first step in the modification. In our case we first calculated the theoretical C/O ratio of a PET monomer. Second, we calculated the theoretical C/O ratios, taking into consideration the introduction of hydroxyl groups in various positions in the PET monomer. Based on our XPS data we calculated the C/O ratios of samples exposed to argon plasma for 1, 3, and 5 minutes. We then compared the theoretical ratio values with the ones obtained experimentally. We found that for plasma exposure of 1 minute the C/O ratio (1.93:1) was very similar to the theoretical ratio obtained when one hydroxyl group was considered to be introduced in the aromatic ring without breaking the aliphatic chain (2:1). Continuing the analysis, it was possible to observe a decrease in our experimental C/O ratios when the plasma treatment was performed for longer periods of time: (1.79:1) after 3min of treatment and (1.69:1) after a 5min exposure. These values presented a reduction of about 30.89% and 34.75%, respectively, in the C/O ratio compared with that of the untreated polyester. Parallel to this, for the theoretical calculation, if we considered the introduction of a second OH group in the aromatic ring, as a result of which the reduction in the C/O ratio compared with that of the original monomer was approximately 33.3%, similar to that of the PET treated for 5 minutes. With these results in mind we believe that the longer the plasma treatment is maintained, the more groups are introduced in the PET chain.

Figure 26 Carbon peaks deconvolution: XPS analysis of one plasma-treated and one untreated fabric. The plasma treatment was carried out at 500mTorr of pressure for 3min. C1s from untreated and treated polyester with argon plasma. It is possible to observe that the proportion between the *various carbons in the chain* was very similar in both the treated (B 5.82:1.91:1) and untreated samples (A 4.42:1.79:1), while the proportion between *carbon* and *oxygen* in the plasma-treated (D) sample compared with that of the untreated sample (C) decreased from approximately 2.6 to 1.8

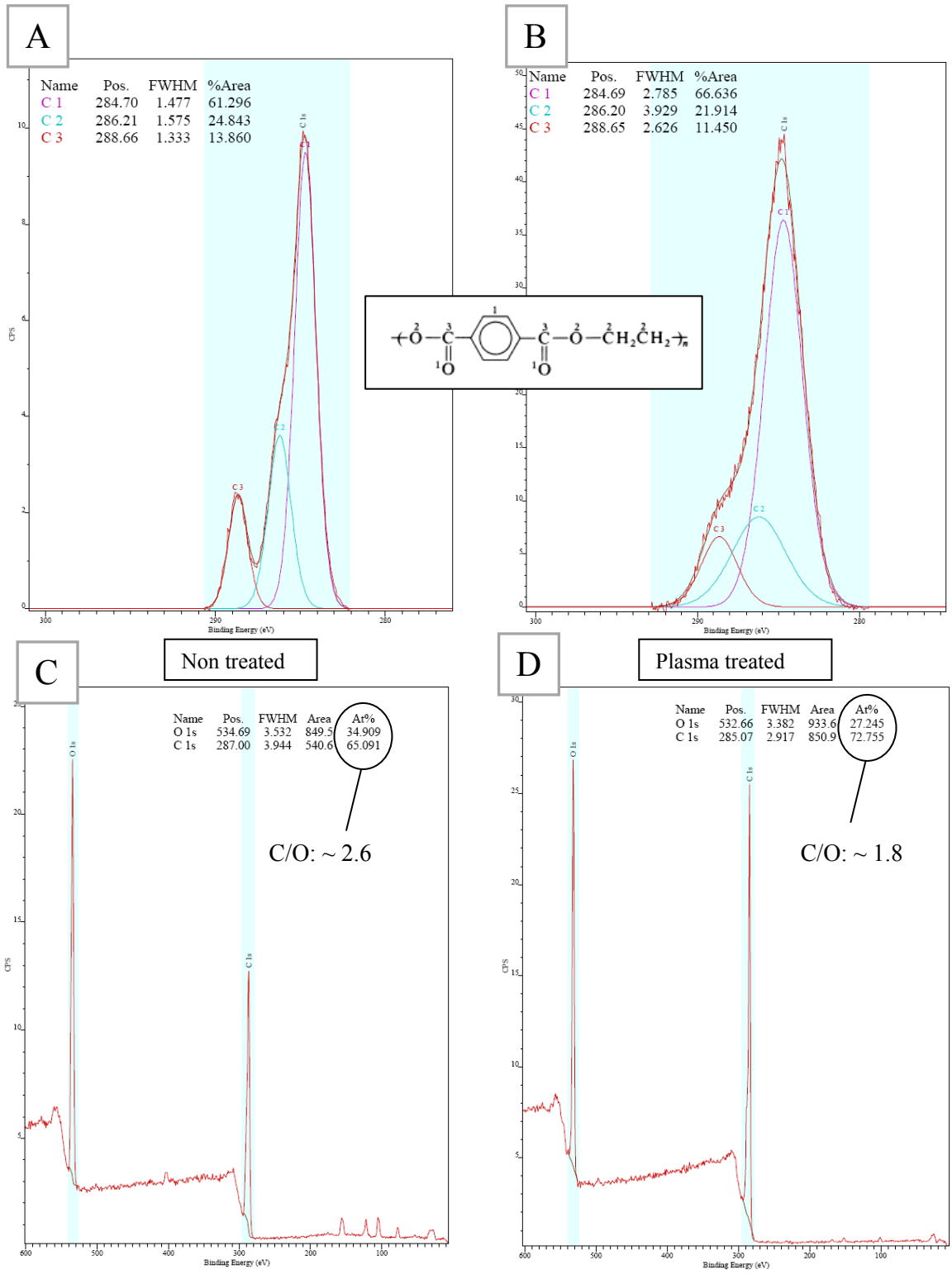
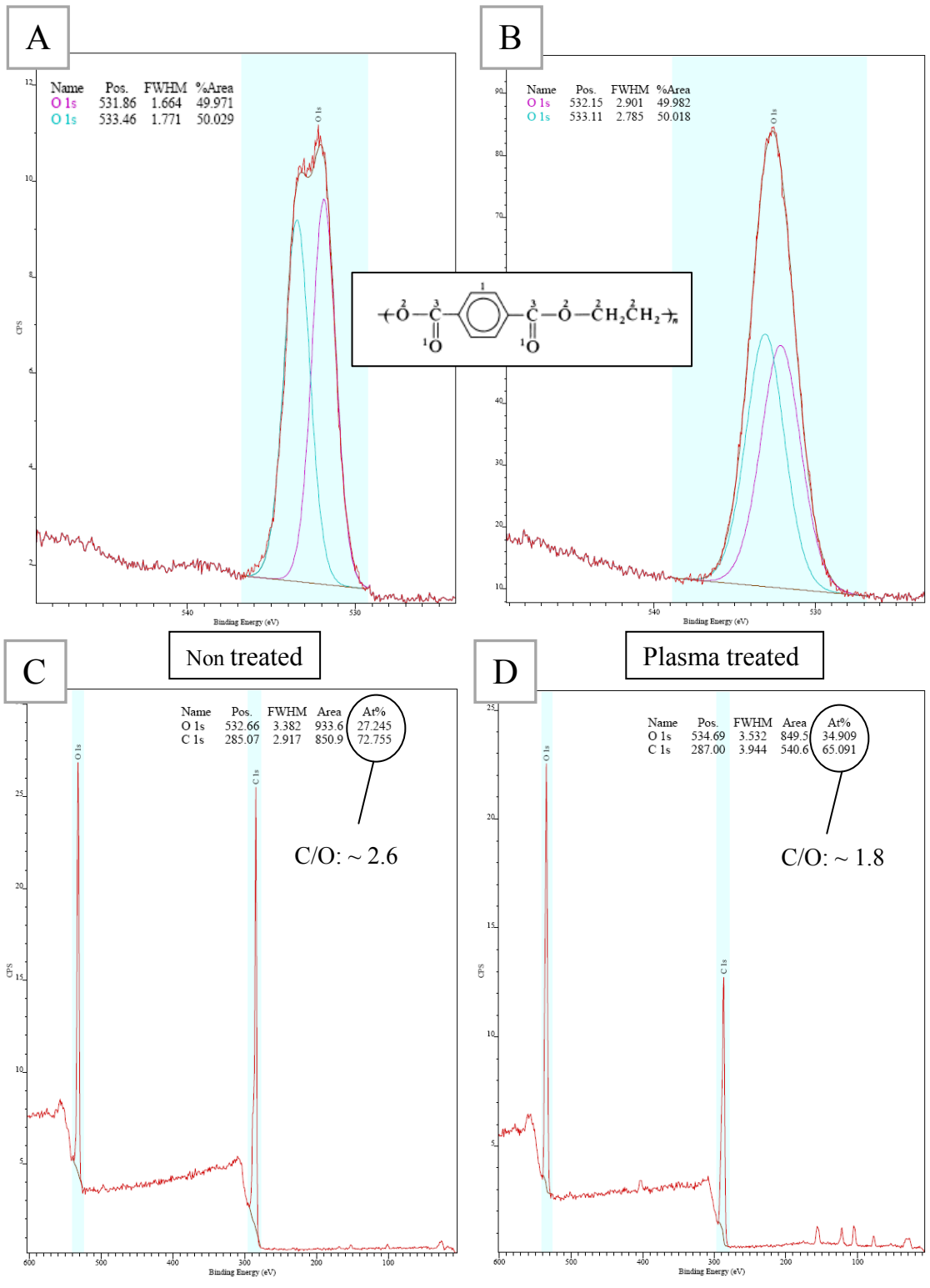

A
Name Pos. FWHM %Area
C 1 284.70 1.477 61.296
C 2 286.21 1.575 24.843
C 3 288.66 1.333 13.860
B
Name Pos. FWHM %Area
C 1 284.69 2.785 66.636
C 2 286.20 3.929 21.914
C 3 288.65 2.626 11.450
Binding Energy (eV)
CPS
Non treated
Plasma treated
C
Name Pos. FWHM Area At%
O 1s 534.69 3.532 849.5 34.909
C 1s 287.00 3.944 540.6 65.091
C/O: ~ 2.6
D
Name Pos. FWHM Area At%
O 1s 532.66 3.382 933.6 27.245
C 1s 285.07 2.917 850.9 72.755
C/O: ~ 1.8

Figure 27 Oxygen peaks deconvolution: XPS analysis of plasma-treated and untreated fabrics. The plasma treatment was carried out at 500mTorr of pressure for 3min. O1s from untreated and treated polyester with argon plasma. It is possible to observe that the proportion between the *two types of oxygen in the chain* was very similar in both the treated (B) and untreated samples (A), while the proportion between *carbon* and *oxygen* in the plasma-treated (D) sample compared with that of the untreated sample (C) decreased from approximately 2.6 to 1.8.


A
Name Pos. FWHM %Area
O 1s 531.86 1.664 49.971
O 1s 533.46 1.771 50.029
B
Name Pos. FWHM %Area
O 1s 532.15 2.901 49.982
O 1s 533.11 2.785 50.018
Non treated
Plasma treated
C
Name Pos. FWHM Area At%
O 1s 532.66 3.382 933.6 27.245
C 1s 285.07 2.917 850.9 72.755
C/O: ~ 2.6
D
Name Pos. FWHM Area At%
O 1s 534.69 3.532 849.5 34.909
C 1s 287.00 3.944 540.6 65.091
C/O: ~ 1.8
Binding Energy (eV)
CPS

Due to its semi-crystalline structure, under plasma treatment polyester could behave as a crystal and use the plasma energy to destroy and rebuild its chain *(52-56)*. The new chain would be a result of the reaction between radicals, low molecular groups that are desorbed from the structure and the components from the air after the exposure. We propose therefore that the steps following the introduction of one single OH group in the chain would be the introduction of more than one hydroxyl group into the polyester structure.

This proposed hypothesis is also in accordance with the XPS analysis of the types of carbon in the chain presented in Figures 26 and 27. We believe that because the OH groups are bonded to the aromatic ring, the carbons in the ring do not respond to a change in electronegativity as the ring becomes stabilized by resonance (20, 34). Even though the percentage of oxygen in the spectrum increased after the plasma treatment, very little modifications were observed in the proportion of areas between the carbon peaks (Figure 26), and in the proportion of areas between the oxygen peaks (Figure 27).

3.3.2 Topographical analysis

The evolution of the topography of the fabric surface before and after the plasma treatment was evaluated under FSEM and AFM. The results are shown in Figure 28.

As seen in the AFM analysis, the untreated fabric presents a relatively smooth surface whereas the treated fabric shows a very irregular surface. This roughness is a result of the etching process in the argon plasma treatment. Similar results have been reported in the literature *(11, 57)*.

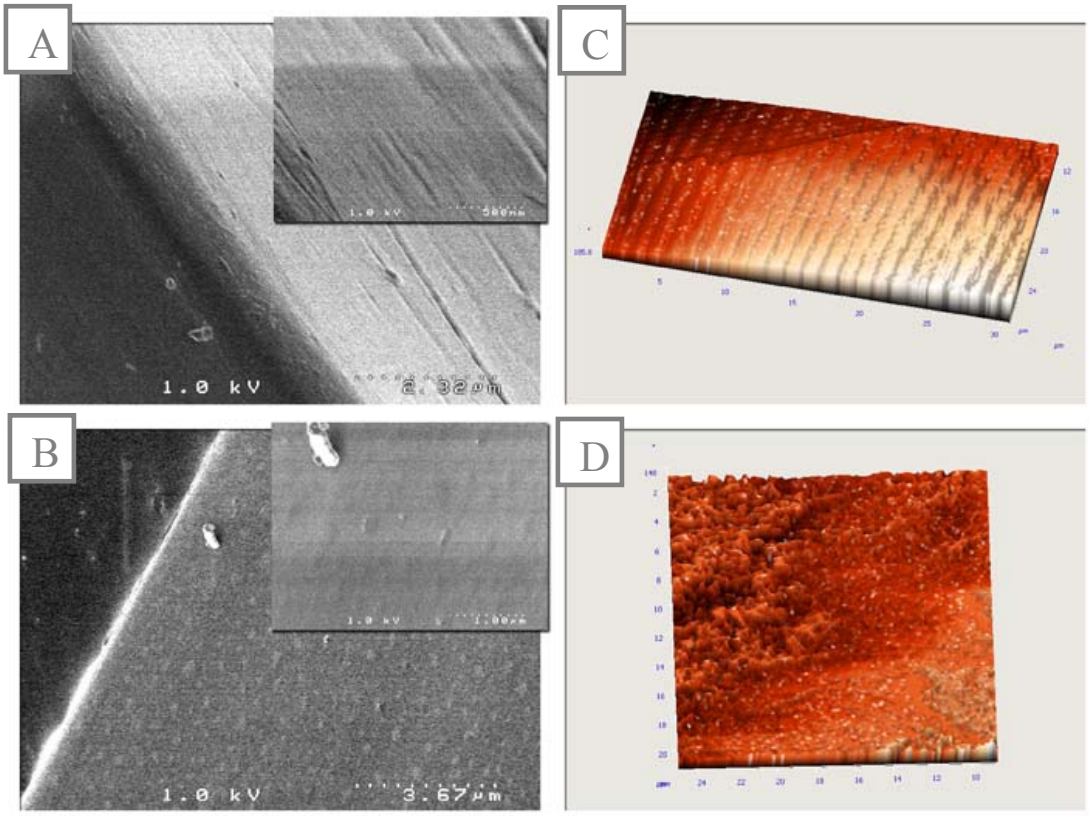


Figure 28 FSEM and AFM analysis of an untreated and treated PET fabric. It is possible to observe the uniformity in the images A and C, which correspond to untreated PET fabric evaluated with FSEM and AFM, respectively. Images B and D show a rough surface. These images correspond to the treated surface.

FSEM imaging was also used to evaluate the texture of the fabric surface. The images presented in Figure 28 are in accordance with the AFM analysis. The untreated PET exhibits a longitudinal pattern over its surface, while in the treated fabric it is possible to perceive an irregular surface. The longitudinal marks in the untreated PET probably result from the extruding process during production. These marks are very regular and cannot be seen in the treated fabric. In the image of the treated polyester it is possible to observe small dots over the entire surface. These dots are very similar to those seen in the image acquired with the AFM, which correspond to the roughness that results from the etching that takes place during the plasma treatment.

3.3.3 Hydrophilicity tests

After plasma treatment, PET fabrics became hydrophilic. Figure 29 shows the results of the hydrophilicity test for both treated and untreated samples.

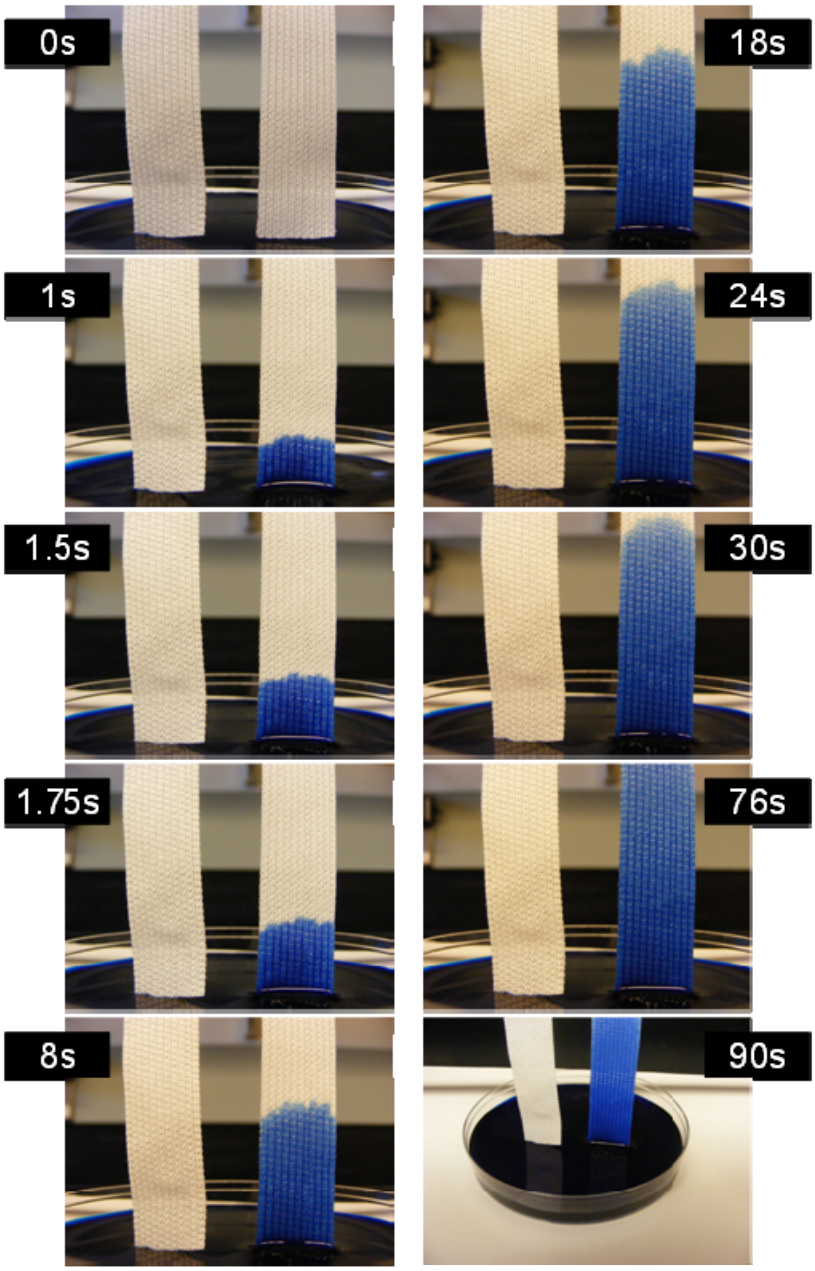


Figure 29 Hydrophilicity test for treated and untreated polyester. The fabrics on the left are untreated and those on the right were treated with argon plasma for 3min. It is possible to observe very little capillary action for the untreated sample, while the plasma-treated fabric completely absorbed the colored water in less than 2min.

3.3.4 Thermosetting

We believe that the plasma treatment introduces not only chemical but also physical modifications in the structure. After thermosetting, the plasma-treated sample became slightly yellow. The differences in the yellow coloration between plasma-treated and untreated fabrics were measured with a spectrophotometer and are presented in Table 4.

Table 4 Spectrophotometer analysis comparing an untreated fabric with a plasma-treated (reference) fabric after thermosetting. It is possible to observe the difference in the yellow range between both samples. A negative value in the yellow-blue range means that the untreated sample was bluer, or that the treated PET was yellower.

	Difference in color	**Lightness**	**+red -green**	**+yellow -blue**	**Color absorption**
Result	1.90	0.40	0.05	-1.54	-1.81

The yellowish color of the plasma-treated samples might have resulted from degradation of the fiber under exposure to high temperature *(47)*. The plasma-treated samples were chemically modified, and could have had their glass transition (Tg) and degradation temperature (Tm) affected as well *(58)*. Therefore, the modified fabric could not resist the effects of lower temperature compared with the untreated polyester, burning faster and turning yellow. Besides the Tg alteration, another hypothesis to explain the observations after thermosetting is based on the plasticizing property of water, which is well known to plasticize fibers during ironing *(59)*. With the plasma-treated polyester, there is a chance that the OH groups created over its surface contributed to plasticizing the fabric. The hydroxyl groups could facilitate the absorption of humidity from the air, which in this case acts as a plasticizer. With the help of a plasticizer the treated fabrics would require lower temperatures or less time in the thermosetting in order to obtain dimensional stability. Therefore, under the same

conditions, a plasma-treated sample could end up degrading and burning while the untreated sample would be affected only in terms of dimensional stability.

3.3.5 Dyeing with reactive dyes

Two types of reactive dyes with low molecular weight were employed. The first was a reactive vinyl sulfone (CI reactive blue 19) with a molecular weight of 659u and the second was a reactive dichlorotriazinyl (CI reactive orange 4) with a molecular weight of 766u, both commonly used over cellulose. Low-molecular-weight reactive dyes were preferred in order to facilitate the diffusion into the fiber *(5)*.

During the dyeing procedure, alkaline pH values facilitate the ionization of cellulose, but also increase the hydrolysis of the dye. As a result, an optimum process should start with a neutral pH, where the dye is absorbed by the fiber (~30min). Furthermore, NaOH is added to enhance fastness, which consists of the reaction between the ionized groups from cellulose with the dye. Considering this theory, we started the dyeing under a neutral pH and after fifteen minutes we added NaOH to adjust the alkaline pH. The pH chosen for the dyeing was based on the acid dissociation constant (pKα) of the reactive groups we believe were being formed over the treated polyester structure. According to the analysis presented in Figure 22, hydroxyl groups were introduced in the aromatic ring of the PET structure. Thus we first chose to dye using a pH based on the pKα of phenol groups (10^{12}) *(60)*, and the first set of experiments—one with the vinyl sulfone dye and the other with the dichlorotriazinyl dye—were realized at a pH of 12. However, predicting the pKα of the new modified fiber could prove to be very difficult, so we decided to test a pH of approximately 10 as well, considered the pKα of methylphenol groups *(61)*. The pH of 10 was tested only in the dyeing process using the dichlorotriazinyl dye.

The results from the dyeing analyzed with a spectrophotometer are presented in Table 5.

Table 5 Spectrophotometer analysis of untreated compared with plasma-treated polyester fabrics after dyeing. The displayed values were analyzed under a blue light. A value with a difference in color greater than 1 means the analyzed color is not the same. The lightness stands for the reflection of light over the fabric. If the analyzed fabric absorbed less color than the one with which it is being compared, it will exhibit a negative value in color absorption and will reflect more light, exhibiting a positive value in luminosity. The color scales +red/-green and +yellow/-blue indicate which color the sample is tending towards.

TYPE OF DYE		**Difference in color**	**Lightness (ΔL)**	**+red -green**	**+yellow -blue**	**Color absorption (ΔC)**
Vinyl sulfone (pH 12)	**Result**	1.81	0.63	0.6	0.52	-0.84
	DevSq	1.20	0.85	0.51	3.45	4.26
Dichlorotriazinyl (pH 12)	**Result**	1.93	0.47	-0.91	-1.36	-1.79
	DevSq	0.13	0.04	0.03	0.06	0.09
Dichlorotriazinyl (pH 10)	**Result**	3.09	0.50	-1.66	-1.56	-2.35
	DevSq	0.77	0.12	0.37	0.30	0.78

The analysis of the three dyeing processes showed a difference in color greater than one, which indicated that the colors were not alike. The difference was visually noticeable. Also, the greater lightness of the untreated fabric compared with that of the treated fabric meant that the treated fabric absorbed more dye. The untreated fabric became less opaque and reflected more light than the treated fabric did—as shown in the luminosity section in the table. Moreover, in accordance with all the other parameters from the spectrophotometer analysis, in the color absorption category the negative value indicated that the untreated fabric absorbed less dye compared with the treated one.

For the dyeing process with vinyl sulphone dye, the positive value in the yellow/blue range means that the treated sample absorbed more blue dye than the untreated fabric did. Still, the difference due to thermosetting is not great, which resulted in a yellowish color on the treated fabric.

In the analysis of the dichlorotriazinyl dye, the negative value in the red/green range indicated that the treated sample absorbed more orange dye than the untreated sample did, while the difference in the yellow scale was due to thermosetting differences. The analysis of the dye yields results similar to those obtained with the process carried out under a pH of 12. However, the numerical differences are greater. For cotton fabrics the pH normally used in industry during the dyeing process is 10. At a pH of 10 the hydroxyl groups from cellulose ionizes forming O^- ions over cellulose. Another parameter influencing the dyeing process is that, under extremely high pH values, reactive dyes tend to hydrolyze. In our case a pH of 10 not only might favor the ionization of the reactive groups over the modified PET, but also its alkalinity did not reach the point at which the dye would hydrolyze.

The differences in color exhibited in the spectrophotometer analysis were assessed after washing the fabrics, which means that the dyes were fastened to the fabrics. It is therefore possible to affirm that plasma-exposed fabrics reacted with the two types of reactive dyes selected, indicating that the plasma treatment imparted modifications introducing hydroxyl groups to the PET structure.

3.4 Conclusions

This study showed that low-pressure plasma treatment can impart important modifications to the polymer structure, improving it not only physically but also chemically during the dyeing process.

Low-pressure argon plasma treatment followed by air exposure can induce chemical and physical modifications over polyester fabrics. XPS analysis complemented with dyeing with reactive dyes showed hydroxyl groups were incorporated into the polymer chains. This was concluded on the basis of the XPS analysis, which showed that the amount of oxygen in the chain increased after treatment without affecting the amount of carbons in the PET structure. The treated fabrics were dyeable with reactive dyes, which remained in the fabric even after washing in boiling water. Fastness is a result of the reaction between the dye and the OH groups over the PET.

The plasma treatment also appeared to have an influence in the thermosetting process previous to dyeing. The treated fabrics plasticized to a greater extent than the untreated fabrics, which could be due to the physical or chemical modification caused in turn by an alteration of the PET's Tg and the introduction of reactive groups in the polymer structure. The hydroxyl groups attached to the polyester chain could absorb water, which in turn would help to plasticize the fabric.

Even though Argon plasma modified the fabric physically, we were able to prove that it chemically improves its dyeability. The plasma treatment increased the dye absorption and altered the PET physically to give an effect of increased depth in color due to irregular reflection from the rough treated surface.

Our study shows therefore that low-pressure plasma treatment can impart important modifications to the polymer structure, not only improving it physically, but also improving it chemically in the dyeing process.

CHAPTER 4: FUTURE WORK

4.1 Evaluation of the penetration of the plasma treatment into a fabric

We were able to prove the presence of hydroxyl groups over a polyester surface using XPS analysis and dyeing methods. We analyzed the efficiency of the reaction between the dye and the OH groups from the fabric by evaluating the fastness of the dyeing process. We washed the dyed polyester under boiling water with soap for 15 minutes. However, we have not evaluated the penetration of the dye into the fabric. We propose an analysis of the dyed samples with a confocal microscope in order to evaluate the penetration of the dye into the layers of the fabric. If a solvent that matches the refractive index of polyester is used under confocal microscopy analysis, we would be able to see only the dye and not the fabric. By changing the focus it would be possible to see if the dye is present in the inner layers of the fabric or only over its surface.

Another way to study the penetration of the plasma treatment is to carry out the plasma experiments over only selected parts of the same piece of textile. The idea would be to cover parts of the fabric and expose them to various treatment times. With this it would be possible to study the diffusion of plasma not only vertically into the fabric but also laterally over the covered parts. XPS analysis and dyeing could be used to evaluate the results of the selective treatment.

4.2 Probing of crystal behavior of polyester under plasma

One of the hypotheses presented as an explanation of the manner in which the oxygen was being attached to the polymer structure was based on the behavior of

crystals in plasmas. We believe that polyester, like crystals, rebuilds its chain while it is being etched during the plasma treatment. This rebuilt chain would result in a new structure containing various reactive groups from the original polymer. In order to prove this theory we propose to conduct plasma treatments for much longer periods. If after the long plasma treatments the fabric maintains its textile characteristics and does not completely degrade, we believe that would show that polyesters behave as crystals under plasma exposure. By measuring the weight of the samples before and after the treatment, it would be possible to determine whether there was any degradation of the polymer resulting in a loss in weight. If the PET does behave as a crystal, its weight should remain the same. The crystallinity of the fabric before and after plasma exposure could be measured with X-Ray Diffraction (XRD).

4.3 Elucidating the influence of thermosetting

We observed that plasma treatment can influence the thermosetting results. Previously, plasma-treated samples plasticized to a greater extent than untreated fabrics after undergoing thermosetting for the same amount of time (30 seconds) and under the same temperature (220°C). However, we do not know if the plasma-treated samples could be plasticized using lower temperatures or for shorter periods of time. Moreover, we do not know if this behavior under thermosetting is a result of the chemical or physical modifications to which the fabrics are subjected under plasma. We propose a broader study of the influence of plasma treatments for the thermosetting of textiles. This study could evaluate the influence of time and temperature combined with DSC analysis of the fabrics in order to observe modifications in thermal properties.

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